



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C03C 25/02, C08J 5/08, H05K 1/03	A1	(11) International Publication Number: WO 00/21899
		(43) International Publication Date: 20 April 2000 (20.04.00)

(21) International Application Number: PCT/US99/21442

(22) International Filing Date: 8 October 1999 (08.10.99)

(30) Priority Data:

09/170,566	13 October 1998 (13.10.98)	US
60/133,076	7 May 1999 (07.05.99)	US
60/146,337	7 July 1999 (07.07.99)	US

(71) Applicant (for all designated States except US): PPG INDUSTRIES OHIO, INC. [US/US]; 3800 West 143rd Street, Cleveland, OH 44111 (US).

(71)(72) Applicants and Inventors: LAWTON, Ernest, L. [US/US]; 3432 Kilcash Drive, Clemmons, NC 27012 (US). WU, Xiang [US/US]; 5165 Amleth Drive, Gibsonia, PA 15044 (US). RICE, William, B. [US/US]; 2855 Gray Moss Drive, Clemmons, NC 27012 (US). NOVICH, Bruce, E. [US/US]; 1035 Highmont Road, Pittsburgh, PA 15232 (US).

(74) Agents: SIMINERIO, Andrew, C.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

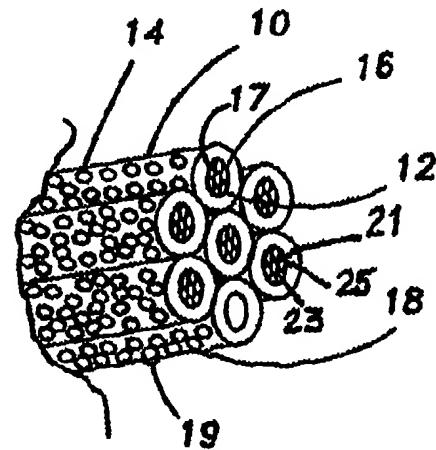
With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: IMPREGNATED GLASS FIBER STRANDS AND PRODUCTS INCLUDING THE SAME

(57) Abstract

The present invention provides a coated fiber strand comprising at least one fiber having a layer of a dried residue of a resin compatible coating composition on at least a portion of a surface of the at least one fiber, the resin compatible coating composition comprising: a) a plurality of discrete, dimensionally stable particles formed from materials selected from the group consisting of organic materials, polymeric materials, composite materials and mixtures thereof that provide an interstitial space between the at least one fiber and at least one adjacent fiber, the particles having an average particle size of about 0.1 to 5 micrometers; b) at least one lubricious material; c) at least one polymeric film former; and d) at least one coupling agent, and a fabric incorporating at least one of the fiber strands.



FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

IMPREGNATED GLASS FIBER STRANDS AND PRODUCTS INCLUDING THE SAME

5

Cross Reference to Related Applications

This patent application is a continuation-in-part application of U.S. Serial No. 09/170,566 of B. Novich et al. entitled "Impregnated Glass Fiber Strands and Products Including the Same" filed on October 13, 1998, which is a continuation-in-part application of U.S. Serial No. 10 09/034,077 of B. Novich et al. entitled "Impregnated Glass Fiber Strands and Products Including the Same" filed March 3, 1998, now abandoned.

This patent application is related to U.S. Patent Application Serial No. 09/170,579 of B. Novich et al. entitled "Methods for Inhibiting Abrasive Wear of Glass Fiber Strands" filed on October 13, 1998, which 15 is a continuation-in-part application of U.S. Application Serial No. 09/034,078 of B. Novich et al. entitled "Methods for Inhibiting Abrasive Wear of Glass Fiber Strands" filed March 3, 1998, now abandoned; U.S. Patent Application Serial No. 09/170,781 of B. Novich et al. entitled "Glass Fiber Strands Coated With Thermally Conductive Inorganic Solid 20 Particles and Products Including the Same" filed on October 13, 1998, which is a continuation-in-part application of U.S. Application Serial No. 09/034,663 of B. Novich et al. entitled "Glass Fiber Strands Coated With Thermally Conductive Inorganic Solid Particles and Products Including the Same" filed March 3, 1998, now abandoned; U.S. Patent Application 25 09/170,780 of B. Novich et al. entitled "Inorganic Lubricant-Coated Glass Fiber Strands and Products Including the Same" filed on October 13, 1998, which is a continuation-in-part application of U.S. Application Serial No. 09/034,525 of B. Novich et al. entitled "Inorganic Lubricant-Coated Glass Fiber Strands and Products Including the Same" 30 filed March 3, 1998, now abandoned; U.S. Patent Application Serial No.

- 2 -

09/170,565 of B. Novich et al. entitled "Inorganic Particle-Coated Glass Fiber Strands and Products Including the Same" filed on October 13, 1998, which is a continuation-in-part application of U.S. Application Serial No. 09/034,056 of B. Novich et al. entitled "Inorganic Particle-Coated

5 Glass Fiber Strands and Products Including the Same" filed March 3, 1998, now abandoned; U.S. Patent Application Serial No. 09/170,578 of B. Novich et al. entitled "Glass Fiber-Reinforced Laminates, Electronic Circuit Boards and Methods for Assembling a Fabric" filed October 13, 1998, which is a continuation-in-part application of U.S. Application Serial

10 No. 09/130,270 of B. Novich et al. entitled "Glass Fiber-Reinforced Laminates, Electronic Circuit Boards and Methods for Assembling a Fabric" filed August 6, 1998, which is a continuation-in-part application of U.S. Serial No. 09/034,525 of B. Novich et al. entitled "Inorganic Lubricant-Coated Glass Fiber Strands and Products Including the Same"

15 filed March 3, 1998, now abandoned.

This application claims the benefit of U.S. Provisional Application Nos. 60/133,076, filed May 7, 1999, and 60/146,337, filed July 30, 1999.

Field of the Invention

20 This invention relates generally to coated fiber strands for reinforcing composites and, more specifically, to glass fiber strands coated with particles that provide interstitial spaces between adjacent glass fibers of the strand.

Background of the Invention

25 In thermosetting molding operations, good "wet-through" (penetration of a polymeric matrix material through the mat or fabric) and "wet-out" (penetration of a polymeric matrix material through the individual bundles or strands of fibers in the mat or fabric) properties are desirable. In contrast,

good dispersion properties are of predominant concern in typical thermoplastic molding operations.

Japanese Patent Application No. 9-208,268 discloses a cloth having yarn formed from glass fibers coated immediately after spinning with starch or

5 a synthetic resin and 0.001 - 20.0 weight percent of inorganic solid particles such as colloidal silica, calcium carbonate, kaolin and talc having average particles sizes of 5 to 2000 nanometers (0.05 to 2 micrometers) to improve resin impregnation. In paragraph 13 of the Detailed Description of the Invention, it is disclosed that such coatings having more than 20 weight

10 percent inorganic solid particles cannot be applied to the glass fiber. Heat or water de-oiling is required prior to formation of a laminate to remove the coating from the glass fibers.

U.S. Patent No. 3,312,569 discloses adhering particles of alumina to the surfaces of the glass fibers to improve penetration of resin between glass

15 reinforcement fibers during formation of a composite. However the Mohs' hardness values for alumina is greater than about 9¹, which can cause abrasion of softer glass fibers.

Soviet Union No. 859400 discloses an impregnating composition for manufacturing laminates of glass fiber cloth, the composition containing an

20 alcoholic solution of phenol-formaldehyde resin, graphite, molybdenum disulphide, polyvinyl butyral and surfactant. Volatile alcoholic solvents are not desirable for glass fiber production applications.

Hollow filler particles can be used to modify the impregnation characteristics of the reinforcing material and/or reduce the overall density of

25 the composite material produced therefrom. For example, US Patent No. 5,412,003 discloses impregnating a glass fiber with a resin composition containing an unsaturated polyester, a polymerizable monomer, a

¹ See R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22, which is hereby incorporated by reference.

thermoplastic resin, a polymerization initiator and hollow glass microspheres (col. 2, lines 6-14). Molding materials and molded products obtained from the impregnated fibers are light in weight (col. 2, lines 26-30). U.S. Patent No. 4,820,575 discloses incorporating hollow body fillers, and particularly heat 5 expandable hollow body fillers, having particle diameters ranging from about 20 to about 300 micrometers into the interspaces between fibers of reinforcing materials to permanently reduce the resin pick up and specific weight of the reinforcing materials (col. 4, lines 39-43 and col. 3, lines 15-30). Preferably, the fillers are applied as an aqueous, binder-free suspension to 10 the reinforcing material (col. 3, lines 63-68 and col. 4, lines 1-3). U.S. Patent No. 5,866,253 discloses incorporating heat expandable hollow particles into fiber strands. The particles are expandable into "microballoons" to create fiber strands having enlarged cross sectional dimensions to be used in composite materials. The expanded particles generally have particle sizes 15 ranging from about 40 to 50 micrometers which is greater than the diameter of the fibers of the strand (col. 3, lines 5-10). Fiber strands having the expanded particles typically have about a four-fold increase in diameter as compared to fibers without the expanded particles and the density of the strand is considerably reduced (col. 4, lines 12-18). The larger strand 20 diameter allows for fewer strands to be used in the formation of composites thereby providing lower finished product density (col. 1, lines 39-43).

In the case of composites or laminates formed from fiber strands woven into fabrics, in addition to providing good wet-through and good wet-out properties of the strands, it is desirable that the coating on the surfaces of 25 the fibers strands protect the fibers from abrasion during processing, provide for good weavability, particularly on air-jet looms and be compatible with the polymeric matrix material into which the fiber strands are incorporated. Many sizing components commonly used on fiber strands to be woven into fabrics can adversely affect adhesion between the glass fibers and the laminate

matrix material. For example, starch, which is a commonly used sizing component for textile fibers, is generally not compatible with laminate resin matrix material. To avoid incompatibility between the glass fibers and the matrix material, the coating or sizing composition is typically removed from

5 the woven cloth prior to lamination by thermal decomposition of the sizing components (called heat cleaning or de-oiling) or by washing the cloth with water (also called de-oiling). A conventional heat cleaning process to thermally decompose sizing components involves heating the cloth at 380°C for 60-80 hours. The heat cleaned cloth is then re-coated with a silane

10 coupling agent to improve adhesion between the glass fiber strands and the matrix material. However, such de-oiling processes are not always completely successful in removing the incompatible materials and can further contaminate the fabric with products of decomposition.

Japanese Patent Application 8-119-682 discloses a primary sizing composition containing a water-soluble epoxy resin that can be easily removed by rinsing with water (page 3, paragraph 2) to improve the removal or de-oiling characteristics of sizing compositions for use in composites. Preferably, the primary sizing comprises an epoxy resin having aggregated and formed particles with diameters of 0.5 to 50 micrometers and a pH

20 between 5.5 and 7.5 (page 4, paragraph 1). Preferably, the epoxy resin is colloid with particles of 1 to 5 micrometers (page 6, paragraph 1). The particles are believed to be beneficial in preventing the flow or migration of the epoxy resin during drying.

U.S. Patent No. 4,009,317 discloses a primary sizing composition containing emulsified clad particles that produce a film on glass fibers and have good burn off characteristics (col. 1, lines 67-68 and col. 2, lines 1-3).

Other patents disclose methods of forming composite material by incorporating particles of polymeric resins into fiber strands and subsequently heating or pressing the strands to form a composite. U.S. Patent No.

4,615,933 discloses saturating glass fabrics or strands with aqueous dispersions of polytetrafluoroethylene or other fluoro-polymer particles to form strands having about 50 to 70 percent by weight fiber and about 30 to 50 percent by weight polytetrafluoroethylene. The strands are subsequently 5 pressed to form composites. U.S. Patent Nos. 5,364,657 and 5,370,911 disclose incorporating polymeric particles into fiber strands by either contacting a moistened strand with a dry polymer particle-laden air stream (col. 2, lines 60-68 and col. 3 lines 1-8 of Patent 5,364,657) or electrostatically adhering polymer particles to a fiber strand (col. 3, lines 13-37 of Patent 10 5,370,911). The fiber strands are then heated to coalesce the particles into continuous polymeric coating that comprises greater than about 10 percent by weight of the coated fiber strand. Other additives such as binders and emulsifiers agents are generally not desirable in the coatings (col. 4, lines 50-51 of Patent 5,370,911 and col. 2, lines 18-21 of Patent 5,364,657). 15 However, coated fiber strands having high levels of polymeric coatings on their surfaces are often difficult to weave on air-jet looms.

There is a need for coatings that inhibit abrasion and breakage of glass fibers, are compatible with a wide variety of polymeric matrix materials and provide for good wet-out and wet-through by the matrix material. In addition, 20 it would be particularly advantageous if the coatings were compatible with modern air-jet weaving equipment to increase productivity.

Summary of the Invention

One aspect of the present invention is a coated fiber strand 25 comprising at least one fiber having a layer of a dried residue of a resin compatible coating composition on at least a portion of a surface of the at least one fiber, the resin compatible coating composition comprising: (a) a plurality of discrete, dimensionally stable particles formed from materials selected from the group consisting of organic materials, polymeric

materials, composite materials and mixtures thereof that provide an interstitial space between the at least one fiber and at least one adjacent fiber, the particles having an average particle size of about 0.1 to about 5 micrometers; (b) at least one lubricious material; (c) at least one polymeric film former; and (d) at least one coupling agent, and a fabric incorporating at least one of the fiber strands.

Another aspect the present invention is a coated fiber strand comprising at least one glass fiber having a dried residue of an aqueous resin compatible coating composition on at least a portion of a surface of the at least one fiber, the aqueous resin compatible coating composition comprising (a) a plurality of discrete, polymeric organic particles that provide an interstitial space between the at least one glass fiber and at least one adjacent glass fiber, the particles having an average particle size of up to about 5 micrometers, (b) a lubricious material selected from the group consisting of oils, waxes, greases and mixtures thereof, (c) polymeric film-forming material selected from the group consisting of thermosetting polymeric materials, thermoplastic polymeric materials, natural polymeric materials and mixtures thereof, and (d) a coupling agent, and a fabric incorporating at least one of the fiber strands.

Still another aspect of the present invention is a coated fiber strand comprising at least one glass fiber having a dried residue of an aqueous resin compatible coating composition on at least a portion of a surface of the at least one fiber, the aqueous resin compatible coating composition comprising: (a) a plurality of particles comprising; (i) at least one particle formed from an acrylic copolymer which is a copolymer of styrene and acrylic; and (ii) at least one particle formed from an inorganic solid lubricant material selected from the group consisting of boron nitride, graphite and metal dichalcogenides, wherein the particles have an average particle size of up to about 5 micrometers and comprise about 35 to about

55 weight percent of the resin compatible coating composition on a total solids basis; (b) a lubricious material selected from the group consisting of cetyl palmitate, cetyl laurate, octadecyl laurate, octadecyl myristate, octadecyl palmitate, octadecyl stearate and paraffin, wherein the

5 lubricious material comprises from about 20 to about 40 weight percent of the resin compatible coating composition on a total solids basis;

10 (c) thermoplastic polymeric film forming material selected from the group consisting of polyvinyl pyrrolidone, polyvinyl alcohol, polyacrylamide, polyacrylic acid and copolymers and mixtures thereof, wherein the

15 thermoplastic polymeric film-forming material comprises about 5 to about 30 weight percent of the resin compatible coating composition on a total solids basis; and (d) a coupling agent, and a fabric incorporating at least one of the fiber strands.

Yet another aspect of the present invention is a fabric comprising a plurality of fibers strands comprising at least one fiber, at least a portion of the fabric having a residue of a resin compatible coating composition comprising: (a) a plurality of discrete, dimensionally stable particles formed from materials selected from the group consisting of organic materials, polymeric materials, composite materials and mixtures thereof that provide an interstitial space between the at least one fiber and at least one adjacent fiber, the particles having an average particle size of about 0.1 to about 5 micrometers; (b) at least one lubricious material; (c) at least one polymeric film former; and (d) at least one coupling agent.

25

Brief Description of the Drawings

The foregoing summary, as well as the following detailed description of the preferred embodiments, will be better understood when read in conjunction with the appended drawings. In the drawings:

Fig. 1 is a perspective view of a coated fiber strand having a primary layer of a dried residue of a coating composition according to the present invention;

5 Fig. 2 is a perspective view of a coated fiber strand having a primary layer of a dried residue of a sizing composition and thereupon a secondary layer of a secondary coating composition according to the present invention;

Fig. 3 is a perspective view of a coated fiber strand having a primary layer of a dried residue of a sizing composition, a secondary layer of a secondary coating composition, and a tertiary layer thereupon according to
10 the present invention;

Fig. 4 is a top plan view of a composite according to the present invention;

Fig. 5 is a top plan view of a fabric according to the present invention;

15 Fig. 6 is a cross-sectional view of an electronic support according to the present invention; and

Figs. 7 and 8 are cross-sectional views of alternate embodiments of an electronic support according to the present invention.

Detailed Description of the Invention

20 The fiber strands of the present invention have a unique coating that not only inhibits abrasion and breakage of the fibers during processing but also provides good wet-through, wet-out and dispersion properties in formation of composites. Good laminate strength, good thermal stability, good hydrolytic stability, low corrosion and reactivity in the presence of high
25 humidity, reactive acids and alkalies and compatibility with a variety of polymeric matrix materials, which can eliminate the need for removing the coating, and in particular heat cleaning, prior to lamination, are other desirable characteristics which are exhibited by the coated fiber strands of the present invention.

Another significant advantage of the coated fiber strands of the present invention is good processability in weaving and knitting. Low fuzz and halos, low broken filaments, low strand tension, high fliability and low insertion time are characteristics provided by the coated glass fiber strands of the present 5 invention that facilitate weaving and knitting and consistently provide a fabric with few surface defects for printed circuit board applications.

Significant advantages of composite materials made from the fiber strands of the present invention include good flexural strength, good interlaminar bond strength and good hydrolytic stability, i.e. resistance to 10 migration of water along the fiber/matrix interface. Additionally, electronic supports and printed circuit boards made from the fiber strands in accordance with the present invention have good drillability and resistance to metal migration (also referred to as cathodic-anodic filament formation or CAF). In particular, printed circuit boards made from the fiber strand in accordance 15 with the present invention have low tool wear during drilling and good locational accuracy of drilled holes.

Referring now to Fig. 1, wherein like numerals indicate like elements throughout, there is shown in Fig. 1 a coated fiber strand 10 comprising a plurality of fibers 12, according to the present invention. As used herein, 20 "strand" means a plurality of individual fibers. The term "fiber" means an individual filament. Although not limiting in the present invention, the fibers 12 typically have an average nominal fiber diameter ranging from about 3 to about 35 micrometers. Preferably the average nominal fiber diameter of the present invention is about 5 micrometers and greater. For "fine yarn" 25 applications, the average nominal fiber diameter preferably ranges from about 5 to about 7 micrometers.

The fibers 12 can be formed from any type of fiberizable material known to those skilled in the art including fiberizable inorganic materials, fiberizable organic materials and mixtures and combinations thereof. The

inorganic and organic materials can be either man-made or naturally occurring materials. One skilled in the art will appreciate that the fiberizable inorganic and organic materials can also be polymeric materials. As used herein the term "polymeric material" means a material formed from

5 macromolecules composed of long chains of atoms that are linked together and that can become entangled in solution or in the solid state². As used herein, the term "fiberizable" means a material capable of being formed into a generally continuous filament, fiber, strand or yarn.

Preferably, the fibers 12 are formed from an inorganic, fiberizable

10 glass material. Fiberizable glass materials useful in the present invention include but are not limited to those prepared from fiberizable glass compositions such as "E-glass", "A-glass", "C-glass", "D-glass", "R-glass", "S-glass", and E-glass derivatives. As used herein, "E-glass derivatives" means glass compositions that include minor amounts of fluorine and/or

15 boron and preferably are fluorine-free and/or boron-free. Furthermore, as used herein, minor means less than about 1 weight percent fluorine and less than about 5 weight percent boron. Basalt and mineral wool are examples of other fiberizable glass materials useful in the present invention. Preferred glass fibers are formed from E-glass or E-glass derivatives. Such

20 compositions are well known to those skilled in the art and further discussion thereof is not believed to be necessary in view of the present disclosure. The glass fibers of the present invention can be formed in any suitable method known in the art, for forming glass fibers. For example, glass fibers can be formed in a direct-melt fiber forming operation or in an indirect, or marble-

25 melt, fiber forming operation. In a direct-melt fiber forming operation, raw materials are combined, melted and homogenized in a glass melting furnace. The molten glass moves from the furnace to a forehearth and into fiber

² James Mark et al. Inorganic Polymers, Prentice Hall Polymer Science and Engineering Series, (1992) at page 1 which is hereby incorporated by reference.

forming apparatuses where the molten glass is attenuated into continuous glass fibers. In a marble-melt glass forming operation, pieces or marbles of glass having the final desired glass composition are preformed and fed into a bushing where they are melted and attenuated into continuous glass fibers. If 5 a premelter is used, the marbles are fed first into the premelter, melted, and then the melted glass is fed into a fiber forming apparatus where the glass is attenuated to form continuous fibers. In the present invention, the glass fibers are preferably formed by the direct-melt fiber forming operation. For additional information relating to glass compositions and methods of forming 10 the glass fibers, see K. Loewenstein, The Manufacturing Technology of Glass Fibres, (3d Ed. 1993) at pages 30-44, 47-103, and 115-165, U.S. Patents 4,542,106 and 5,789,329, and IPC-EG-140 "Specification for Finished Fabric Woven from 'E' Glass for Printed Boards" at page 1, a publication of The Institute for Interconnecting and Packaging Electronic Circuits (June 1997), 15 which are hereby incorporated by reference.

Non-limiting examples of suitable non-glass fiberizable inorganic materials include ceramic materials formed from silicon carbide, carbon, graphite, mullite, aluminum oxide and piezoelectric ceramic materials. Non-limiting examples of suitable fiberizable organic materials include cotton, 20 cellulose, natural rubber, flax, ramie, hemp, sisal and wool. Non-limiting examples of suitable fiberizable organic polymeric materials include those formed from polyamides (such as nylon and aramids), thermoplastic polyesters (such as polyethylene terephthalate and polybutylene terephthalate), acrylics (such as polyacrylonitriles), polyolefins, polyurethanes 25 and vinyl polymers (such as polyvinyl alcohol). Non-glass fiberizable material useful in the present invention and methods for preparing and processing such fibers are discussed at length in the Encyclopedia of Polymer Science and Technology, Vol. 6 (1967) at pages 505-712, which is hereby incorporated by reference. It is understood that blends or copolymers of any

of the above materials and combinations of fibers formed from any of the above materials can be used in the present invention, if desired.

The present invention will now be discussed generally in the context of glass fiber strands, although one skilled in the art would understand that the 5 strand 10 can comprise fibers 12 formed from any fiberizable material known in the art as discussed above.

With continued reference to Fig. 1, in a preferred embodiment, at least one and preferably all of the fibers 12 of fiber strand 10 of the present invention have a layer 14 of a residue of a coating composition on at least a 10 portion 17 of the surfaces 16 of the fibers 12 to protect the fiber surfaces 16 from abrasion during processing and inhibit fiber breakage. Preferably, the layer 14 is present on the entire outer surface 16 or periphery of the fibers 12.

The coating compositions of the present invention are preferably aqueous coating compositions and more preferably aqueous, resin 15 compatible coating compositions. Although not preferred for safety reasons, the coating compositions can contain volatile organic solvents such as alcohol or acetone as needed, but preferably are free of such solvents. Additionally, the coating compositions of the present invention can be used as primary sizing compositions and/or secondary sizing or coating compositions.

20 As used herein, in a preferred embodiment the terms "size", "sized" or "sizing" refer to a coating composition applied to the fibers. The terms "primary size" or "primary sizing" refer to the coating composition applied to the fibers immediately after formation of the fibers. The terms "secondary size", "secondary sizing" or "secondary coating" mean coating compositions 25 applied to the fibers after the application of a primary size. This coating can be applied to the fiber before the fiber is incorporated into a fabric or it can be applied to the fiber after the fiber is incorporated into a fabric, e.g. by coating the fabric. In an alternative embodiment, the terms "size", "sized" or "sizing" additionally refer to a coating composition (also known as a "finishing size")

applied to the fibers after at least a portion, and typically all of a conventional, non-resin compatible sizing composition has been removed by heat or chemical treatment, i.e., the finishing size is applied to bare glass fibers incorporated into a fabric form.

5 As used herein, the term "resin compatible" means the coating composition applied to the glass fibers is compatible with the polymeric matrix material into which the glass fibers will be incorporated such that the coating composition (or selected coating components) does not require removal prior to incorporation into the matrix material (such as by heat cleaning), facilitates

10 good wet-out and wet-through of the matrix material during processing and results in composite materials having desired physical properties and hydrolytic stability.

The coating composition of the present invention comprises one or more, and preferably a plurality of particles 18 that when applied to at least one fiber 23 of the plurality of fibers 12 adheres to the outer surface 16 of the at least one fiber 23 and provides one or more interstitial spaces 21 between adjacent glass fibers 23, 25 of the strand 10. These interstitial spaces 21 correspond generally to the average size 19 of the particles 18 positioned between the adjacent fibers.

20 The particles 18 of the present invention are preferably discrete particles. As used herein the term "discrete" means that the particles do not tend to coalesce or combine to form films under processing conditions, but instead generally retained their individual shape or form. In addition, the particles are preferably dimensionally stable. As used herein the term

25 "dimensionally stable particles" means that the particles will generally maintain their average particle size and shape under processing conditions, such as the forces generated between adjacent fibers during weaving, roving and other processing operations, so as to maintain the desired interstitial spaces between adjacent fibers 23, 25. In other words, the particles

preferably will not crumble, dissolve or substantially deform in the coating composition to form a particle having a maximum dimension less than its selected average particle size under typical glass fiber processing conditions, such as exposure to temperatures of up to about 25°C and preferably up to 5 about 100°C, and more preferably up to about 140°C. Additionally, the particles 18 should not substantially enlarge or expand in size under glass fiber processing conditions and, more particularly, under composite processing conditions where the processing temperatures can exceed 150°C. As used herein, the phrase "should not substantially enlarge in size" in 10 reference to the particles means that the particles should not expand or increase in size to more than approximately 3 times their initial size during processing. Preferably, the coating compositions of the present invention are essentially free of heat expandable hollow particles. As used herein, the term "heat expandable hollow particles" means hollow particles filled with or 15 containing a blowing agent, which when exposed to temperatures sufficient to volatilize the blowing agent expand or substantially enlarge in size. As used herein the term "essentially free of" means the sizing composition comprises less than about 20 weight percent of heat expandable hollow particles on a total solids basis, more preferably less than about 5 weight percent, and most 20 preferably less than 0.001 weight percent. Furthermore, as used herein, the term "dimensionally stable" includes both crystalline and non-crystalline materials.

In addition, although not required, it is preferred that the particles 18 are non-waxy. The term "non-waxy" means the materials from which the 25 particles are formed are not wax-like. As used herein, the term "wax-like" means materials composed primarily of unentangled hydrocarbons chains

having an average carbon chain length ranging from about 25 to about 100 carbon atoms^{3,4}.

Preferably, the particles 18 in the present invention are discrete, dimensionally stable, non-waxy particles.

5 The particles 18 can have any shape or configuration desired.

Although not limiting in the present invention, examples of suitable particle shapes include spherical (such as beads, microbeads or hollow spheres), cubic, platy or acicular (elongated or fibrous). Additionally, the particles 18 can have an internal structure that is hollow, porous or void free, or a

10 combination thereof. In addition, the particles 18 can have a combination of these structures, e.g. a hollow center with porous or solid walls. For more information on suitable particle characteristics see H. Katz et al. (Ed.), Handbook of Fillers and Plastics, (1987) at pages 9-10 which are hereby incorporated by reference.

15 The particles 18 can be formed from materials selected from the group consisting of polymeric and non-polymeric inorganic materials, polymeric and non-polymeric organic materials, composite materials and mixtures thereof. As used herein the term "polymeric inorganic material" means a polymeric material having a backbone repeat unit based on an element or elements 20 other than carbon. For more information see J. E. Mark et al. at page 5, which is hereby incorporated by reference. Polymeric organic materials include synthetic polymeric materials, semisynthetic polymeric materials and natural polymeric materials. An "organic material", as used herein, means all compounds of carbon except such binary compounds as the carbon oxides, 25 the carbides, carbon disulfide, etc.; such ternary compounds as the metallic cyanides, metallic carbonyls, phosgene, carbonyl sulfide, etc.; and metallic

³ L. H. Sperling Introduction of Physical Polymer Science, John Wiley and Sons, Inc. (1986) at pages 2-5, which are hereby incorporated by reference.

carbonates, such as calcium carbonate and sodium carbonate. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at pages 761-762 which are hereby incorporated by reference. More generally, organic materials include carbon containing compounds wherein the carbon is

5 typically bonded to itself and to hydrogen, and often to other elements as well and excludes carbon-containing ionic compounds. See M. Silberberg, Chemistry The Molecular Nature of Matter and Change, (1996) at page 586, which is hereby incorporated by reference. The term "inorganic material" generally means all materials that are not compounds of carbon with the

10 exception of carbon oxides and carbon disulfide. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 636 which are hereby incorporated by reference. As used herein the term "inorganic materials" means any material that is not an organic material. As used here in the term "composite material" means a combination of two or more different

15 materials. For more information on particles useful in the present invention, see G. Wypych, Handbook of Fillers, 2nd Ed. (1999) at pages 15-202, which are hereby incorporated by reference.

Non-polymeric, inorganic materials useful in forming the particles 18 of the present invention include inorganic materials selected from the group

20 consisting of metals, oxides, carbides, nitrides, borides, sulfides, silicates, carbonates, sulfates and hydroxides. A non-limiting example of a suitable inorganic nitride from which the particles 18 are formed is boron nitride, which is the preferred inorganic material from which particles 18 useful in the present invention are formed. A non-limiting example of a useful inorganic

25 oxide is zinc oxide. Suitable inorganic sulfides include molybdenum disulfide, tantalum disulfide, tungsten disulfide and zinc sulfide. Useful inorganic silicates include aluminum silicates and magnesium silicates, such as

⁴ W. Pushaw, et al. "Use of Micronised Waxes and Wax Dispersions in Waterborne Systems" Polymers, Paint, Colours Journal, V.189, No. 4412 January 1999 at pages 18-21 which are

vermiculite. Suitable metals include molybdenum, platinum, palladium, nickel, aluminum, copper, gold, iron, silver and alloys and mixtures thereof.

Although not required, the particles 18 are formed from solid lubricant materials. As used herein the term "solid lubricant" means any solid used

- 5 between two surfaces to provide protection from damage during relative movement and/or to reduce friction and wear. In one embodiment, the solid lubricants are inorganic solid lubricants. As used herein, "inorganic solid lubricant" means that the solid lubricants have a characteristic crystalline habit which causes them to shear into thin, flat plates which readily slide over
- 10 one another and thus produce an antifriction lubricating effect between the glass fiber surface and an adjacent solid surface, at least one of which is in motion. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 712, which is hereby incorporated by reference. Friction is the resistance to sliding one solid over another. F. Clauss, Solid Lubricants
- 15 and Self-Lubricating Solids, (1972) at page 1, which is hereby incorporated by reference.

In one embodiment of the present invention, the solid lubricant materials have a lamellar structure. Solid lubricants having a lamellar structure are composed of sheets or plates of atoms in hexagonal array, with

- 20 strong bonding within the sheet and weak van der Waals bonding between sheets, providing low shear strength between sheets. A non-limiting example of a lamellar structure is a hexagonal crystal structure. K. Ludema Friction, Wear, Lubrication (1996) at page 125, Solid Lubricants and Self-Lubricating Solids at pages 19-22, 42-54, 75-77, 80-81, 82, 90-102, 113-120 and 128,
- 25 and W. Campbell "Solid Lubricants", Boundary Lubrication; An Appraisal of World Literature, ASME Research Committee on Lubrication (1969) at pages 202-203, which are hereby incorporated by reference. Inorganic solid

particles having a lamellar fullerene structure are also useful in the present invention.

Non-limiting examples of suitable inorganic solid lubricant materials having a lamellar structure that are useful in forming the particles 18 of the present invention include boron nitride, graphite, metal dichalcogenides, mica, talc, gypsum, kaolinite, calcite, cadmium iodide, silver sulfide and mixtures thereof. Preferred inorganic solid lubricant materials include boron nitride, graphite, metal dichalcogenides and mixtures thereof. Suitable metal dichalcogenides include molybdenum disulfide, molybdenum diselenide, tantalum disulfide, tantalum diselenide, tungsten disulfide, tungsten diselenide and mixtures thereof.

A non-limiting example of an inorganic solid lubricant material for use in the coating composition of the present invention having a hexagonal crystal structure is boron nitride. Particles formed from boron nitride, zinc sulfide and montmorillonite also provide good whiteness in composites with polymeric matrix materials such as nylon 6,6.

Non-limiting examples of particles formed from boron nitride that are suitable for use in the present invention are PolarTherm® 100 Series (PT 120, PT 140, PT 160 and PT 180), 300 Series (PT 350) and 600 Series (PT 620, PT 630, PT 640 and PT 670) boron nitride powder particles which are commercially available from Advanced Ceramics Corporation of Lakewood, Ohio. "PolarTherm® Thermally Conductive Fillers for Polymeric Materials" a technical bulletin of Advanced Ceramics Corporation of Lakewood, Ohio (1996), which is hereby incorporated by reference. These particles have a thermal conductivity of about 250-300 Watts per meter °K at 25°C, a dielectric constant of about 3.9 and a volume resistivity of about 10^{15} ohm-centimeters. The 100 Series powder particles have an average particle size ranging from about 5 to about 14 micrometers, the 300 Series powder particles have an average particle size ranging from about 100 to about 150 micrometers and

the 600 Series powder particles have an average particle size ranging from about 16 to greater than about 200 micrometers.

In another embodiment of the present invention, the particles 18 are formed from inorganic solid lubricant materials that are non-hydratable. As used herein, "non-hydratable" means that the solid inorganic lubricant particles do not react with molecules of water to form hydrates and contain water of hydration or water of crystallization. A "hydrate" is produced by the reaction of molecules of water with a substance in which the H-OH bond is not split. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at pages 609-610 and T. Perros, Chemistry, (1967) at pages 186-187, which are hereby incorporated by reference. Hydrates contain coordinated water, which coordinates the cations in the hydrated material and cannot be removed without the breakdown of the structure, and/or structural water, which occupies interstices in the structure to add to the electrostatic energy without upsetting the balance of charge. R. Evans, An Introduction to Crystal Chemistry, (1948) at page 276, which is hereby incorporated by reference. Preferably, the coating composition is essentially free of hydratable inorganic solid lubricants. As used herein the term "essentially free of" means the coating composition comprises less than about 20 weight percent of hydratable inorganic lubricant particles on a total solids basis, more preferably less than about 5 weight percent, and most preferably less than 0.001 weight percent.

While not preferred, the coating compositions according to the present invention can contain particles formed from hydratable or hydrated inorganic solid lubricant materials in addition to the non-hydratable inorganic solid lubricant materials discussed above. Non-limiting examples of such hydratable inorganic solid lubricant materials are clay mineral phyllosilicates, including micas (such as muscovite), talc, montmorillonite, kaolinite and gypsum.

The particles 18 can be formed from non-polymeric, organic materials. Examples of non-polymeric, organic materials useful in the present invention include but are not limited to stearates (such as zinc stearate and aluminum stearate), carbon black and stearamide.

5 The particles 18 can be formed from inorganic polymeric materials. Non-limiting examples of useful inorganic polymeric materials include polyphosphazenes, polysilanes, polysiloxane, polygermanes, polymeric sulfur, polymeric selenium, silicones and mixtures thereof. A specific, non-limiting example of a particle formed from an inorganic polymeric material 10 suitable for use in the present invention is Tospearl⁵, which is a particle formed from cross-linked siloxanes and is commercially available from Toshiba Silicones Company, Ltd. of Japan.

15 Suitable synthetic, organic polymeric materials from which the particles can be formed include, but are not limited to, thermosetting materials and thermoplastic materials. Suitable thermosetting materials include thermosetting polyesters, vinyl esters, epoxy materials, phenolics, aminoplasts, thermosetting polyurethanes and mixtures thereof. A specific, non-limiting example of a preferred synthetic polymeric particle formed from an epoxy material is an epoxy microgel particle.

20 Suitable thermoplastic materials include thermoplastic polyesters, polycarbonates, polyolefins, acrylic polymers, polyamides, thermoplastic polyurethanes, vinyl polymers and mixtures thereof. Preferred thermoplastic polyesters include but are not limited to polyethylene terephthalate, polybutylene terephthalate and polyethylene naphthalate. Preferred 25 polyolefins include but are not limited to polyethylene, polypropylene and polyisobutene. Preferred acrylic polymers include copolymers of styrene and acrylic and polymers containing methacrylate. Non-limiting examples of

⁵ See R. J. Perry "Applications for Cross-Linked Siloxane Particles" Chemtech, February 1999 at pages 39-44.

synthetic polymeric particles formed from an acrylic copolymer are ROPAQUE® HP-1055⁶, which is an opaque, non-film-forming, styrene acrylic polymeric synthetic pigment having a 1.0 micrometer particle size, a solids content of 26.5 percent by weight and a 55 percent void volume, ROPAQUE®

5 OP-96⁷, which is an opaque, non-film-forming, styrene acrylic polymeric synthetic pigment dispersion having a particle size of 0.55 micrometers and a solids content of 30.5 percent by weight, and ROPAQUE® OP-62 LO⁸ which is also an opaque, non-film-forming, styrene acrylic polymeric synthetic pigment dispersion having a particles size of 0.40 micrometers and a solids

10 content of about 36.5 percent by weight, each of which are commercially available from Rohm and Haas Company of Philadelphia, PA.

Suitable semisynthetic, organic polymeric materials from which the particles 18 can be formed include but are not limited to cellulosics, such as methylcellulose and cellulose acetate; and modified starches, such as starch

15 acetate and starch hydroxyethyl ethers.

Suitable natural polymeric materials from which the particles 18 can be formed include but are not limited to polysaccharides, such as starch; polypeptides, such as casein; and natural hydrocarbons, such as natural rubber and gutta percha.

20 In one embodiment of the present invention, the polymeric particles 18 are formed from hydrophobic polymeric materials to reduce or limit moisture absorption by the coated strand. Non-limiting examples of hydrophobic polymeric materials believed to be useful in the present invention include but are not limited to polyethylene, polypropylene, polystyrene and

⁶ See product property sheet entitled: "ROPAQUE® HP-1055, Hollow Sphere Pigment for Paper and Paperboard Coatings" October 1994, available from Rohm and Haas Company, Philadelphia, PA at page 1 which is hereby incorporated by reference.

⁷ See product technical bulletin entitled: "Architectural Coatings- ROPAQUE® OP-96, The All Purpose Pigment", April 1997 available from Rohm and Haas Company, Philadelphia, PA at page 1 which is hereby incorporated by reference.

⁸ Ibid.

polymethylmethacrylate. Non-limiting examples of polystyrene copolymers include ROPAQUE® HP-1055, ROPAQUE® OP-96, and ROPAQUE® OP-62 LO pigments (each discussed above).

In another embodiment of the present invention, polymeric particles 18 5 are formed from polymeric materials having a glass transition temperature (T_g) and/or melting point greater than about 25°C and preferably greater than about 50°C.

Composite particles 18 useful in the present invention include particles formed by cladding, encapsulating or coating particles formed from a primary 10 material with one or more secondary materials. For example, an inorganic particle formed from an inorganic material such as silicon carbide or aluminum nitride can be provided with a silica, carbonate or nanoclay coating to form a useful composite particle. In another example, a silane coupling agent with alkyl side chains can be reacted with the surface of an inorganic 15 particle formed from an inorganic oxide to provide a useful composite particle having a "softer" surface. Other examples include cladding, encapsulating or coating particles formed from organic or polymeric materials with inorganic materials or different organic or polymeric materials. A specific non-limiting example of such composite particles is DUALITE, which is a synthetic 20 polymeric particle coated with calcium carbonate that is commercially available from Pierce and Sevens Corporation of Buffalo, NY.

In still another embodiment of the present invention, the particles 18 can be hollow particles formed from materials selected from the group 25 consisting of inorganic materials, organic materials, polymeric materials, composite materials and mixtures thereof. Non-limiting examples of suitable materials from which the hollow particles can be formed are described above. Non-limiting examples of a hollow polymeric particle useful in present invention are ROPAQUE® HP-1055, ROPAQUE® OP-96 and ROPAQUE® OP-62 LO pigments (each discussed above). For other non-limiting

examples of hollow particles that can be useful in the present invention see H. Katz et al. (Ed.) (1987) at pages 437-452 which are hereby incorporated by reference.

The particles 18 can be present in a dispersion, suspension or emulsion in water. Other solvents, such as mineral oil or alcohol (preferably less than about 5 weight percent), can be included in the dispersion, suspension or emulsion, if desired. A non-limiting example of a preferred dispersion of particles formed from an inorganic material is ORPAC BORON NITRIDE RELEASECOAT-CONC, which is a dispersion of about 25 weight percent boron nitride particles in water and is commercially available from ZYP Coatings, Inc. of Oak Ridge, Tennessee. "ORPAC BORON NITRIDE RELEASECOAT-CONC", a technical bulletin of ZYP Coatings, Inc., is hereby incorporated by reference. The boron nitride particles in this product have an average particle size of less than about 3 micrometers and include about 1 percent of magnesium-aluminum silicate to bind the boron nitride particles to the substrate to which the dispersion is applied. Other useful products which are commercially available from ZYP Coatings include BORON NITRIDE LUBRICOAT® paint, and BRAZE STOP and WELD RELEASE products. Specific, non-limiting examples of emulsions and dispersions of synthetic polymeric particles formed from acrylic polymers and copolymers include: Rhoplex® GL-623⁹ which is an all acrylic firm polymer emulsion having a solids content of 45 percent by weight and a glass transition temperature of about 98°C; EMULSION E-2321¹⁰ which is a hard, methacrylate polymer emulsion having a solids content of 45 percent by weight and a glass transition temperature of about 105°C; ROPAQUE® OP-96 (discussed

⁹ See product property sheet entitled: "Rhoplex® GL-623, Self-Crosslinking Acrylic Binder of Industrial Nonwovens", March 1997 available from Rohm and Haas Company, Philadelphia, PA which is hereby incorporated by reference.

¹⁰ See product property sheet entitled: "Building Products Industrial Coatings- Emulsion E-2321", 1990, available from Rohm and Haas Company, Philadelphia, PA which is hereby incorporated by reference.

above), which is supplied as a dispersion having a particle size of 0.55 micrometers and a solids content of 30.5 percent by weight; ROPAQUE® OP-62 LO (discussed above), which is also a opaque, non-film-forming synthetic pigment dispersion having a particles size of 0.40 micrometers and

5 a solids content of about 36.5 percent by weight; and ROPAQUE® HP-1055 (discussed above), which is supplied as a dispersion having a solids content of about 26.5 percent by weight; all of which are commercially available from Rohm and Haas Company of Philadelphia, PA.

The particles 18 are selected to have a average particle size 19

10 sufficient to effect the desired spacing between adjacent fibers. For example, the average size 19 of the particles 18 incorporated into a sizing composition applied to fibers 12 to be processed on air-jet looms is preferably selected to provide sufficient spacing between adjacent fibers to permit air-jet transport of the fiber strand 10 across the loom. As used herein, "air-jet loom" means a

15 type of loom in which the fill yarn (weft) is inserted into the warp shed by a blast of compressed air from one or more air jet nozzles. In another example, the average size 19 of the particles 18 incorporated into a sizing composition applied to fibers 12 to be impregnated with a polymeric matrix material is selected to provide sufficient spacing between adjacent fibers to permit good

20 wet-out and wet-through of the fiber strand 10.

In a specific, non-limiting embodiment of the present invention, the average particle size 19 of the particles 18 is at least about 0.1 micrometers, preferably at least about 0.5 micrometers, and ranges from about 0.1 micrometers to about 5 micrometers and preferably from about 0.5

25 micrometers to about 2.0 micrometers. In this embodiment, the particles 18 have an average particle sizes 19 that is generally smaller than the average diameter of the fibers 12 to which the coating composition is applied. It has been observed that twisted yarns made from fiber strands 10 having a layer 14 of a residue of a primary sizing composition comprising particles 18 having

average particles sizes 19 discussed above can provide sufficient spacing between adjacent fibers 23, 25 to permit air-jet weavability (i.e. air-jet transport across the loom) while maintaining the integrity of the fiber strand 10 and providing acceptable "wet-through" and "wet-out" characteristics when 5 impregnated with a polymeric matrix material.

In another specific, non-limiting embodiment of the present invention the average particles size 19 of particles 18 is at least 3 micrometers, preferably at least about 5 micrometers, and ranges from 3 to about 1000 micrometers, preferably about 5 to about 1000 micrometers, and more 10 preferably about 10 to about 25 micrometers. Preferably, each of the particles 18 has a minimum particle size of at least 3 micrometers, and preferably of at least about 5 micrometers. It is also preferred in this embodiment that the average particle size 19 of the particles 18 corresponds generally to the average nominal diameter of the glass fibers. It has been 15 observed that fabrics made with strands coated with the particles of the sizes as discussed above exhibit good "wet-through" and "wet-out" characteristics when impregnated with a polymeric matrix material.

It will be recognized by one skilled in the art that mixtures of one or more particles 18 having different average particle sizes 19 can be 20 incorporated into the sizing composition in accordance with the present invention to impart the desired properties and processing characteristics to the fiber strands 10 and to the products subsequently made therefrom. More specifically, different sized particles can be combined in required amounts so as provide fibers having good air-jet transport properties as well a fabric 25 exhibiting good wet-out and wet-through characteristics.

Glass fibers are subject to abrasive wear by contact with asperities of adjacent glass fibers and/or other solid objects or materials which the glass fibers contact during forming and subsequent processing, such as weaving or roving. "Abrasive wear", as used herein, means scraping or cutting off of bits

of the glass fiber surface or breakage of glass fibers by frictional contact with particles, edges or entities of materials which are hard enough to produce damage to the glass fibers. See K. Ludema at page 129, which is hereby incorporated by reference. Abrasive wear of glass fiber strands causes

5 strand breakage during processing and surface defects in products such as woven cloth and composites, which increases waste and manufacturing cost.

To minimize abrasive wear, in one embodiment of the present invention, the particles 18 have a hardness value which does not exceed, i.e., is less than or equal to, a hardness value of the glass fiber(s). The hardness

10 values of the particles and glass fibers can be determined by any conventional hardness measurement method, such as Vickers or Brinell hardness, but is preferably determined according to the original Mohs' hardness scale which indicates the relative scratch resistance of the surface of a material. The Mohs' hardness value of glass fibers generally ranges from 15 about 4.5 to about 6.5, and is preferably about 6. R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22, which is hereby incorporated by reference. In this embodiment, the Mohs' hardness value of the particles 18 preferably ranges from about 0.5 to about 6. The Mohs' hardness values of several non-limiting examples of particles formed from 20 inorganic materials suitable for use in the present invention are given in Table A below.

Table A

Particle material	Mohs' hardness (original scale)
boron nitride	about 2 ¹¹
graphite	about 0.5-1 ¹²
molybdenum disulfide	about 1 ¹³
talc	about 1-1.5 ¹⁴
mica	about 2.8-3.2 ¹⁵
kaolinite	about 2.0-2.5 ¹⁶
gypsum	about 1.6-2 ¹⁷
calcite (calcium carbonate)	about 3 ¹⁸
calcium fluoride	about 4 ¹⁹
zinc oxide	about 4.5 ²⁰
aluminum	about 2.5 ²¹
copper	about 2.5-3 ²²
iron	about 4-5 ²³
gold	about 2.5-3 ²⁴
nickel	about 5 ²⁵
palladium	about 4.8 ²⁶
platinum	about 4.3 ²⁷
silver	about 2.5-4 ²⁸

¹¹ K. Ludema, Friction, Wear, Lubrication, (1996) at page 27, which is hereby incorporated by reference.

¹² R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22.

¹³ R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 793, which is hereby incorporated by reference.

¹⁴ Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 1113, which is hereby incorporated by reference.

¹⁵ Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 784, which is hereby incorporated by reference.

¹⁶ Handbook of Chemistry and Physics at page F-22.

¹⁷ Handbook of Chemistry and Physics at page F-22.

¹⁸ Friction, Wear, Lubrication at page 27.

¹⁹ Friction, Wear, Lubrication at page 27.

²⁰ Friction, Wear, Lubrication at page 27.

²¹ Friction, Wear, Lubrication at page 27.

²² Handbook of Chemistry and Physics at page F-22.

²³ Handbook of Chemistry and Physics at page F-22.

²⁴ Handbook of Chemistry and Physics at page F-22.

²⁵ Handbook of Chemistry and Physics at page F-22.

²⁶ Handbook of Chemistry and Physics at page F-22.

²⁷ Handbook of Chemistry and Physics at page F-22.

²⁸ Handbook of Chemistry and Physics at page F-22.

In another embodiment of the present invention, the particles 18 are thermally conductive, i.e., have a thermal conductivity greater than about 30 Watts per meter K, such as for example boron nitride, graphite, and the metallic inorganic solid lubricants discussed above. The thermal conductivity 5 of a solid material can be determined by any method known to one skilled in the art, such as the guarded hot plate method according to ASTM C-177-85 (which is hereby incorporated by reference) at a temperature of about 300K.

In yet another embodiment of the present invention, the particles 18 are electrically insulative or have high electrical resistivity, i.e., have an 10 electrical resistivity greater than about 1000 microohm-cm, such as for example boron nitride.

The particles 18 can comprise about 1 to about 80 weight percent of the coating composition on a total solids basis, preferably about 1 to about 60 weight percent. In one embodiment, the coating composition contains about 15 20 to about 60 weight percent of particles 18 on total solids basis, and preferably about 35 to about 55 weight percent, and more preferably about 30 to about 50 weight percent.

It will be appreciated by one skilled in the art that discrete particles 18 of the coating composition can include any combination or mixture of particles 20 18 discussed above. More specifically, the particles 18 can include additional discrete particles made from any of the materials described above for forming the particles 18 in an amount less than the particles 18. These additional particles are different from the other particles 18 in the resin compatible coating composition, i.e. the addition particles (1) are chemically different 25 from the other particles; or (2) are chemically the same but different in configuration or properties. The additional particles can comprise up to half of the particles 18, preferably up to about 15 percent of the particles 18.

In addition to the particles, the coating composition preferably comprises one or more polymeric film-forming materials, such as organic,

inorganic and natural polymeric materials. Useful organic polymeric materials include but are not limited to synthetic polymeric materials, semisynthetic polymeric materials, natural polymeric materials and mixtures thereof.

Synthetic polymeric materials include but are not limited to thermoplastic

- 5 materials and thermosetting materials. Preferably the polymeric film-forming materials form a generally continuous film when applied to the surface 16 of the glass fibers. Generally, the amount of polymeric film-forming materials can range from about 1 to about 60 weight percent of the coating composition on a total solids basis, preferably about 5 to about 50 weight percent, and
- 10 more preferably about 10 to about 30 weight percent.

In one embodiment of the present invention, thermosetting polymeric film-forming materials are the preferred polymeric film-forming materials for use in the coating composition for coating glass fiber strands. Such materials are compatible with thermosetting matrix materials used as laminates for

- 15 printed circuit boards, such as FR-4 epoxy resins, which are polyfunctional epoxy resins and in one particular embodiment of the invention is a difunctional brominated epoxy resins. See Electronic Materials HandbookTM, ASM International (1989) at pages 534-537, which are hereby incorporated by reference.

- 20 Useful thermosetting materials include thermosetting polyesters, epoxy materials, vinyl esters, phenolics, aminoplasts, thermosetting polyurethanes and mixtures thereof. Suitable thermosetting polyesters include STYPOL polyesters that are commercially available from Cook Composites and Polymers of Port Washington, Wisconsin and NEOXIL polyesters that are
- 25 commercially available from DSM B.V. of Como, Italy.

A non-limiting example of a thermosetting polymeric material is an epoxy material. Useful epoxy materials contain at least one epoxy or oxirane group in the molecule, such as polyglycidyl ethers of polyhydric alcohols or thiols. Examples of suitable epoxy film-forming polymers include EPON® 826

and EPON® 880 epoxy resins, which are commercially available from Shell Chemical Company of Houston, Texas.

Useful thermoplastic polymeric materials include vinyl polymers, thermoplastic polyesters, polyolefins, polyamides (e.g. aliphatic polyamides or 5 aromatic polyamides such as aramid), thermoplastic polyurethanes, acrylic polymers (such as polyacrylic acid) and mixtures thereof.

In another embodiment of the present invention, the preferred polymeric film-forming material is a vinyl polymer. Useful vinyl polymers in the present invention include, but are not limited to, polyvinyl pyrrolidones such 10 as PVP K-15, PVP K-30, PVP K-60 and PVP K-90, each of which is commercially available from ISP Chemicals of Wayne, New Jersey. Other suitable vinyl polymers include Resyn 2828 and Resyn 1037 vinyl acetate copolymer emulsions which are commercially available from National Starch Starch and Chemical of Bridgewater, New Jersey, other polyvinyl acetates 15 such as are commercially available from H. B. Fuller and Air Products and Chemicals Company of Allentown, Pennsylvania, and polyvinyl alcohols which are also available from Air Products and Chemicals Company.

Thermoplastic polyesters useful in the present invention include DESMOPHEN 2000 and DESMOPHEN 2001KS, both of which are 20 commercially available from Bayer of Pittsburgh, Pennsylvania. Preferred polyesters include RD-847A polyester resin which is commercially available from Borden Chemicals of Columbus, Ohio, and DYNAKOLL SI 100 resin which is commercially available from Eka Chemicals AB, Sweden. Useful polyamides include the VERSAMID products that are commercially available 25 from General Mills Chemicals, Inc. Useful thermoplastic polyurethanes include WITCOBOND® W-290H, which is commercially available from Witco Chemical Corp. of Chicago, Illinois, and RUCOTHANE® 2011L polyurethane latex, which is commercially available from Ruco Polymer Corp. of Hicksville, New York.

The aqueous sizing composition of the present invention can comprise a mixture of one or more thermosetting polymeric materials with one or more thermoplastic polymeric materials. In one embodiment of the present invention particularly useful for laminates for printed circuit boards, the

5 polymeric materials of the aqueous sizing composition comprise a mixture of RD-847A polyester resin, PVP K-30 polyvinyl pyrrolidone, DESMOPHEN 2000 polyester and VERSAMID polyamide. In an alternative embodiment suitable for laminates for printed circuit boards, the polymeric materials of the aqueous sizing composition comprise PVP K-30 polyvinyl pyrrolidone,

10 optionally combined EPON 826 epoxy resin.

Semisynthetic polymeric materials suitable for use as polymeric film-formers include but are not limited to cellulosics such as hydroxypropylcellose and modified starches such as KOLLOTEX 1250 (a low viscosity, low amylose potato-based starch etherified with ethylene oxide) which is

15 commercially available from AVEBE of the Netherlands

Natural polymeric materials suitable for use as polymeric film-formers include but are not limited to starches prepared from potatoes, corn, wheat, waxy maize, sago, rice, milo and mixtures thereof.

It should be appreciated that depending on the nature of the starch,

20 the starch can function as both a particle 18 and/or a film former. More specifically, some starches will dissolve completely in a solvent, and in particular water, and function as a film forming material while others will not completely dissolve and will maintain a particular grain size and function as a particle 18. Although starches (both natural and semisynthetic) can be used

25 in accordance with the present invention, the coating composition of the present invention is preferably essentially free of starch materials. As used herein the term "essentially free of starch materials" means that the coating composition comprises less than 20 weight percent on a total solids basis of the coating composition, preferably less than 5 weight percent and more

preferably is free of starch materials. Primary sizing compositions containing starches that are applied to fiber strands to be incorporated into laminates for printed circuit boards are typically not resin compatible and must be removed prior to incorporation into the polymeric matrix material. As previously

5 discussed, preferably the coating compositions of the present invention are resin compatible and do not require removal. More preferably, the coating compositions of the present invention are compatible with matrix materials used to make printed circuit boards (discussed below) and most preferably are epoxy resin compatible.

10 The polymeric film-forming materials can be water soluble, emulsifiable, dispersible and/or curable. As used herein, "water soluble" means that the polymeric materials are capable of being essentially uniformly blended and/or molecularly or ionically dispersed in water to form a true solution. See Hawley's at page 1075, which is hereby incorporated by reference. "Emulsifiable" means that the polymeric materials are capable of forming an essentially stable mixture or being suspended in water in the presence of an emulsifying agent. See Hawley's at page 461, which is hereby incorporated by reference. Non-limiting examples of suitable emulsifying agents are set forth below. "Dispersible" means that any of the

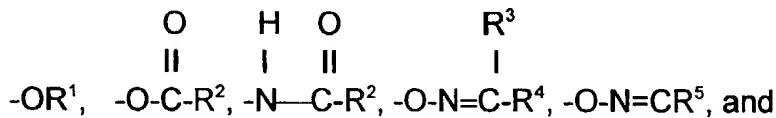
15 components of the polymeric materials are capable of being distributed throughout water as finely divided particles, such as a latex. See Hawley's at page 435, which is hereby incorporated by reference. The uniformity of the dispersion can be increased by the addition of wetting, dispersing or emulsifying agents (surfactants), which are discussed below. "Curable"

20 means that the polymeric materials and other components of the sizing composition are capable of being coalesced into a film or crosslinked to each other to change the physical properties of the polymeric materials. See Hawley's at page 331, which is hereby incorporated by reference.

25

In addition to or in lieu of the polymeric film forming materials discussed above, the coating composition preferably comprises one or more glass fiber coupling agents such as organo-silane coupling agents, transition metal coupling agents, phosphonate coupling agents, aluminum coupling agents, amino-containing Werner coupling agents and mixtures thereof.

These coupling agents typically have dual functionality. Each metal or silicon atom has attached to it one or more groups which can either react with or compatibilize the fiber surface and/or the components of the resin matrix. As used herein, the term "compatibilize" means that the groups are chemically attracted, but not bonded, to the fiber surface and/or the components of the coating composition, for example by polar, wetting or solvation forces. In one nonlimiting embodiment, each metal or silicon atom has attached to it one or more hydrolyzable groups that allow the coupling agent to react with the glass fiber surface, and one or more functional groups that allow the coupling agent to react with components of the resin matrix. Examples of hydrolyzable groups include:



the monohydroxy and/or cyclic $\text{C}_2\text{-C}_3$ residue of a 1,2- or 1,3 glycol, wherein R^1 is $\text{C}_1\text{-C}_3$ alkyl; R^2 is H or $\text{C}_1\text{-C}_4$ alkyl; R^3 and R^4 are independently selected from H, $\text{C}_1\text{-C}_4$ alkyl or $\text{C}_6\text{-C}_8$ aryl; and R^5 is $\text{C}_4\text{-C}_7$ alkylene. Examples of suitable compatibilizing or functional groups include epoxy, glycidoxyl, mercapto, cyano, allyl, alkyl, urethano, halo, isocyanato, ureido, imidazolinyl, vinyl, acrylato, methacrylato, amino or polyamino groups.

Functional organo-silane coupling agents are preferred for use in the present invention. Examples of useful functional organo silane coupling agents include gamma-aminopropyltrialkoxysilanes, gamma-isocyanatopropyltriethoxysilane, vinyl-trialkoxysilanes,

glycidoxypropyltrialkoxysilanes and ureidopropyltrialkoxysilanes. Preferred functional organo-silane coupling agents include A-187 gamma-glycidoxypropyltrimethoxysilane, A-174 gamma-methacryloxypropyltrimethoxysilane, A-1100 gamma-aminopropyltriethoxysilane silane coupling agents, A-1108 5 amino silane coupling agent and A-1160 gamma-ureidopropyltriethoxysilane (each of which are commercially available from Witco Corporation OSi Specialties, Inc. of Tarrytown, New York). The organo silane coupling agent can be at least partially hydrolyzed with water prior to application to the fibers, preferably at about a 1:1 stoichiometric ratio or, if desired, applied in 10 unhydrolyzed form. The pH of the water can be modified by the addition of an acid or a base to initiate or speed the hydrolysis of the coupling agent as is well known in the art.

Suitable transition metal coupling agents include titanium, zirconium, yttrium and chromium coupling agents. Suitable titanate coupling agents and 15 zirconate coupling agents are commercially available from Kenrich Petrochemical Company. Suitable chromium complexes are commercially available from E.I. duPont de Nemours of Wilmington, Delaware. The amino-containing Werner-type coupling agents are complex compounds in which a trivalent nuclear atom such as chromium is coordinated with an organic acid 20 having amino functionality. Other metal chelate and coordinate type coupling agents known to those skilled in the art can be used herein.

The amount of coupling agent can range from about 1 to about 30 weight percent of the coating composition on a total solids basis, preferably about 1 to about 10 weight percent, and more preferably about 2 to about 8 25 weight percent.

The coating composition can further comprise one or more softening agents or surfactants that impart a uniform charge to the surface of the fibers causing the fibers to repel from each other and reducing the friction between the fibers, so as to function as a lubricant. Although no required, preferably

the softening agents are chemically different from other components of the coating composition. Such softening agents include cationic, non-ionic or anionic softening agents and mixtures thereof, such as amine salts of fatty acids, alkyl imidazoline derivatives such as CATION X, which is commercially

5 available from Rhone Poulenc of Princeton, New Jersey, acid solubilized fatty acid amides, condensates of a fatty acid and polyethylene imine and amide substituted polyethylene imines, such as EMERY® 6717, a partially amidated polyethylene imine commercially available from Henkel Corporation of Kankakee, Illinois. While the coating composition can comprise up to about

10 60 weight percent of softening agents, preferably the coating composition comprises less than about 20 weight percent and more preferably less than about 5 weight percent of the softening agents. For more information on softening agents, see A. J. Hall, Textile Finishing, 2nd Ed. (1957) at pages 108-115, which are hereby incorporated by reference.

15 The coating composition can further include one or more lubricious materials that are chemically different from the polymeric materials and softening agents discussed above to impart desirable processing characteristics to the fiber strands during weaving. Suitable lubricious materials can be selected from the group consisting of oils, waxes, greases

20 and mixtures thereof. Non-limiting examples of wax materials useful in the present invention include aqueous soluble, emulsifiable or dispersible wax materials such as vegetable, animal, mineral, synthetic or petroleum waxes, e.g. paraffin. Oils useful in the present invention include both natural oils, semisynthetic oils and synthetic oils. Generally, the amount of wax or other

25 lubricious material can range from 0 to about 80 weight percent of the sizing composition on a total solids basis, preferably from about 1 to about 50 weight percent, more preferably from about 20 to about 40 weight percent, and most preferably from about 25 to about 35 weight percent.

Preferred lubricious materials include waxes and oils having polar characteristics, and more preferably include highly crystalline waxes having polar characteristics and melting points above about 35°C and more preferably above about 45°C. Such materials are believed to improve the

5 wet-out and wet-through of polar resins on fiber strands coated with sizing compositions containing such polar materials as compared to fiber strands coated with sizing compositions containing waxes and oils that do not have polar characteristics. Preferred lubricious materials having polar characteristics include esters formed from reacting (1) a monocarboxylic acid

10 and (2) a monohydric alcohol. Non-limiting examples of such fatty acid esters useful in the present invention include cetyl palmitate, which is preferred (such as is available from Stepan Company of Maywood, New Jersey as KESSCO 653 or STEPANTEX 653), cetyl myristate (also available from Stepan Company as STEPANLUBE 654), cetyl laurate, octadecyl laurate,

15 octadecyl myristate, octadecyl palmitate and octadecyl stearate. Other fatty acid ester, lubricious materials useful in the present invention include trimethylolpropane tripelargonate, natural spermaceti and triglyceride oils, such as but not limited to soybean oil, linseed oil, epoxidized soybean oil, and epoxidized linseed oil.

20 While not preferred, the coating composition can include one or more other lubricious materials, such as non-polar petroleum waxes, in lieu of or in addition to of those lubricious materials discussed above. Non-limiting examples of non-polar petroleum waxes include MICHEM® LUBE 296 microcrystalline wax, POLYMEKON® SPP-W microcrystalline wax and

25 PETROLITE 75 microcrystalline wax which are commercially available from Michelman Inc. of Cincinnati, Ohio and the Petrolite Corporation of Tulsa, Oklahoma, respectively.

Although not required, if desired the coating composition can also include a resin reactive diluent to further improve lubrication of the coated

fiber strands of the present invention and provide good processability in weaving and knitting by reducing the potential for fuzz, halos and broken filaments during such manufacturing operations, while maintaining resin compatibility. As used herein, "resin reactive diluent" means that the

5 diluent includes functional groups that are capable of chemically reacting with the same resin with which the coating composition is compatible. The diluent can be any lubricant with one or more functional groups that react with a resin system, preferably functional groups that react with an epoxy resin system, and more preferably functional groups that react with

10 an FR-4 epoxy resin system. Non-limiting examples of suitable lubricants include lubricants with amine groups, alcohol groups, anhydride groups, acid groups or epoxy groups. A non-limiting example of a lubricant with an amine group is a modified polyethylene amine, e.g. EMERY 6717, which is a partially amidated polyethylene imine commercially available

15 from Henkel Corporation of Kankakee, Illinois. A non-limiting example of a lubricant with an alcohol group is polyethylene glycol, e.g. CARBOWAX 300, which is a polyethylene glycol that is commercially available from Union Carbide of Danbury, Connecticut. A non-limiting example of a lubricant with an acid group is fatty acids, e.g. stearic acid and salts of

20 stearic acids. Non-limiting examples of lubricants with an epoxy group include epoxidized soybean oil and epoxidized linseed oil, e.g. FLEXOL LOE, which is an epoxidized linseed oil, and FLEXOL EPO, which is an epoxidized soybean oil, both commercially available from Union Carbide of Danbury, Connecticut, and LE-9300 epoxidized silicone emulsion, which is

25 commercially available from Witco Corporation OSi Specialties, Inc. of Danbury, Connecticut. Although not limiting in the present invention, the sizing composition can include a resin reactive diluent as discussed above in an amount up to about 15 weight percent of the sizing composition on a total solids basis.

The coating composition can include one or more emulsifying agents for emulsifying or dispersing components of the sizing composition, such as the particles 18 and/or lubricious materials. Non-limiting examples of suitable emulsifying agents or surfactants include polyoxyalkylene block copolymers

5 (such as PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey), ethoxylated alkyl phenols (such as IGEPAL CA-630 ethoxylated octylphenoxyethanol which is commercially available from GAF Corporation of Wayne, New Jersey), polyoxyethylene octylphenyl glycol ethers, ethylene

10 oxide derivatives of sorbitol esters (such as TMAZ 81 which is commercially available BASF of Parsippany, New Jersey), polyoxyethylated vegetable oils (such as ALKAMULS EL-719, which is commercially available from Rhone-Poulenc), ethoxylated alkylphenols (such as MACOL OP-10 which is also commercially available from BASF) and nonylphenol surfactants (such as

15 MACOL NP-6 which is also commercially available from BASF). Generally, the amount of emulsifying agent can range from about 1 to about 30 weight percent of the coating composition on a total solids basis, preferably from about 1 to about 15 weight percent.

Crosslinking materials, such as melamine formaldehyde, and

20 plasticizers, such as phthalates, trimellitates and adipates, can also be included in the coating composition. The amount of crosslinker or plasticizer can range from about 1 to about 5 weight percent of the coating composition on a total solids basis.

Other additives can be included in the coating composition, such as

25 silicones, fungicides, bactericides and anti-foaming materials, generally in an amount of less than about 5 weight percent. Organic and/or inorganic acids or bases in an amount sufficient to provide the coating composition with a pH of about 2 to about 10 can also be included in the coating composition. A non-limiting example of a suitable silicone emulsion is LE-9300 epoxidized

silicone emulsion, which is commercially available from Witco Corporation OSi Specialties, Inc. of Danbury, Connecticut. An example of a suitable bactericide is Biomet 66 antimicrobial compound, which is commercially available from M & T Chemicals of Rahway, New Jersey. Suitable anti-5 foaming materials are the SAG materials, which are commercially available from OSi Specialties, Inc. of Danbury, Connecticut and MAZU DF-136, which is available from BASF Company of Parsippany, New Jersey. Ammonium hydroxide can be added to the coating composition for coating stabilization, if desired. Preferably water and more preferably deionized water is included 10 in the coating composition in an amount sufficient to facilitate application of a generally uniform coating upon the strand. The weight percentage of solids of the coating composition generally ranges from about 1 to about 20 weight percent.

The coating composition is preferably essentially free of glass 15 materials. As used herein, "essentially free of glass materials" means that the sizing composition comprises less than 20 volume percent of glass matrix materials for forming glass composites, preferably less than about 5 volume percent, and more preferably is free of glass materials. Examples of such glass matrix materials include black glass ceramic matrix materials or 20 aluminosilicate matrix materials such as are well known to those skilled in the art.

In one embodiment for weaving fabric for laminated printed circuit boards, glass fibers of the coated fiber strand of the present invention have a primary layer of a dried residue of an aqueous primary sizing composition 25 comprising ROPAQUE® HP-1055 or ROPAQUE® OC-96 styrene acrylic polymeric synthetic pigments, PVP K-30 polyvinyl pyrrolidone, A-174 acrylic-functional organo silane coupling agents and A-187 epoxy-functional organo silane coupling agents, EMERY® 6717 partially amidated polyethylene imine, STEPANTEX 653 cetyl palmitate, TMAZ 81 ethylene oxide derivatives of

sorbitol esters, MACOL OP-10 ethoxylated alkylphenol and MAZU DF-136 anti-foaming material.

In another preferred embodiment for weaving fabric for laminated printed circuit boards, glass fibers of the coated fiber strand of the present

5 invention have applied thereto a primary layer of a dried residue of an aqueous primary sizing composition comprising ROPAQUE® HL-1055 or ROPAQUE® OC-96 styrene-acrylic copolymer hollow spheres, PolarTherm® 160 boron nitride powder and/or ORPAC BORON NITRIDE RELEASECOAT-CONC dispersion, PVP K-30 polyvinyl pyrrolidone, A-174 acrylic-functional

10 organo silane coupling agents and A-187 epoxy-functional organo silane coupling agents, EMERY® 6717 partially amidated polyethylene imine, STEPANTEX 653 cetyl palmitate, TMAZ 81 ethylene oxide derivatives of sorbitol esters, MACOL OP-10 ethoxylated alkylphenol, and MAZU DF-136 anti-foaming material.

15 While not preferred, fiber strands having a residue of a coating composition similar to those described above that are free of particles 18 can be made in accordance with the present invention. In particular, it is contemplated that aqueous, resin compatible sizing compositions including one or more film-forming polymeric materials, such as PVP K-30 polyvinyl pyrrolidone; one or more silane coupling agents, such as A-174 acrylic-functional organo silane coupling agents and A-187 epoxy-functional organo silane coupling agents; and at least about 25 percent by weight of the sizing composition on a total solids basis of a lubricious material having polar characteristics, such as STEPANTEX 653 cetyl palmitate, can be made in

20 accordance with the present invention. It will be further appreciated by those skilled in the art that fiber strands having a residue of an aqueous, resin compatible sizing composition that is essentially free of particles 18 can be woven into fabrics and made into electronic supports and electronic circuit boards (as described below) in accordance with the present invention.

25

The coating compositions of the present invention can be prepared by any suitable method such as conventional mixing well known to those skilled in the art. Preferably the components discussed above are diluted with water to have the desired weight percent solids and mixed together. The particles

5 18 can be premixed with water, emulsified or otherwise added to one or more components of the coating composition prior to mixing with the remaining components of the coating.

Sizing compositions according to the present invention can be applied in many ways, for example by contacting the filaments with a roller or belt

10 applicator, spraying or other means. The sized fibers are preferably dried at room temperature or at elevated temperatures. The dryer removes excess moisture from the fibers and, if present, cures any curable sizing composition components. The temperature and time for drying the glass fibers will depend upon such variables as the percentage of solids in the sizing

15 composition, components of the sizing composition and type of glass fiber.

The amount of the coating composition present as a dried residue on the fiber strand is preferably less than about 30 percent by weight, more preferably less than about 10 percent by weight and most preferably less than about 5 percent by weight as measured by loss on ignition (LOI). In one

20 embodiment of the invention, the LOI is less than 1 percent by weight. As used herein the term "loss on ignition" means the weight percent of dried coating composition present on the surface of the fiber strand as determined by the following equation (Eq.1):

$$LOI = 100 \times [(W_{dry} - W_{bare})/W_{dry}] \quad \text{Eq. 1}$$

25 wherein W_{dry} is the weight of the fiber strand plus the residue of the coating composition after drying in an oven at about 220°F (about 104°C) for about 60 minutes and W_{bare} is the weight of the bare fiber strand after removal of residue of the coating composition by heating the fiber strand in an oven at about 1150°F (about 621°C) for about 20 minutes.

After the application of the primary size, the fibers are gathered into strands having 2 to about 15,000 fibers per strand, and preferably about 100 to about 1600 fibers per strand..

A secondary layer of a secondary sizing or secondary coating

- 5 composition can be applied over the primary layer in an amount effective to coat or impregnate the portion of the strands, for example by dipping the coated strand in a bath containing the secondary coating composition, spraying the secondary coating composition upon the coated strand or by contacting the coated strand with an applicator as discussed above. The
- 10 coated strand can be passed through a die to remove excess coating composition from the strand and/or dried as discussed above for a time sufficient to at least partially dry or cure the secondary coating composition. The method and apparatus for applying the secondary coating composition to the strand is determined in part by the configuration of the strand material.
- 15 The strand is preferably dried after application of the secondary coating composition in a manner well known in the art.

Suitable secondary coating compositions can include one or more film-forming materials, lubricants and other additives such as are discussed above. The secondary coating is preferably different from the primary sizing

- 20 composition, i.e. it (1) contains at least one component which is chemically different from the components of the sizing composition; or (2) contains at least one component in an amount which is different from the amount of the same component contained in the sizing composition. Non-limiting examples of suitable secondary coating compositions including polyurethane are
- 25 disclosed in U.S. Patent Nos. 4,762,750 and 4,762,751, which are hereby incorporated by reference.

Referring now to Fig. 2, in an alternative embodiment according to the present invention, the glass fibers 212 of the coated fiber strand 210 can having applied thereto a primary layer 214 of a dried residue of a primary

sizing composition which can include any of the sizing components in the amounts discussed above. Examples of suitable sizing compositions are set forth in Loewenstein at pages 237-291 (3d Ed. 1993) and U.S. Patent Nos. 4,390,647 and 4,795,678, each of which is hereby incorporated by reference.

- 5 A secondary layer 215 of a secondary coating composition is applied to at least a portion, and preferably over the entire outer surface, of the primary layer 214. The secondary coating composition comprises one or more types of discrete particles 216 such as are discussed in detail above. The amount of particles in the secondary coating composition can range from about 1 to
- 10 about 99 weight percent on a total solids basis and preferably about 20 to about 90 weight percent. The percentage of solids of the aqueous secondary coating composition generally ranges from about 5 to about 50 weight percent.

In an alternative embodiment, the particles of the secondary coating composition comprise hydrophilic inorganic solid particles that absorb and retain water in the interstices of the hydrophilic particles. The hydrophilic inorganic solid particles can absorb water or swell when in contact with water or participate in a chemical reaction with the water to form, for example, a viscous gel-like solution which blocks or inhibits further ingress of water into the interstices of a telecommunications cable which the coated glass fiber strand is used to reinforce. As used herein, "absorb" means that the water penetrates the inner structure or interstices of the hydrophilic material and is substantially retained therein. See Hawley's Condensed Chemical Dictionary at page 3, which is hereby incorporated by reference. "Swell" means that the hydrophilic particles expand in size or volume. See Webster's New Collegiate Dictionary (1977) at page 1178, which is hereby incorporated by reference. Preferably, the hydrophilic particles swell after contact with water to at least one and one-half times their original dry weight, and more preferably about two to about six times their original weight. Non-limiting examples of

hydrophilic inorganic solid lubricant particles that swell include smectites such as vermiculite and montmorillonite, absorbent zeolites and inorganic absorbent gels. Preferably, these hydrophilic particles are applied in powder form over tacky sizing or other tacky secondary coating materials. The 5 amount of hydrophilic inorganic particles in this embodiment of the secondary coating composition can range from about 1 to about 99 weight percent on a total solids basis and preferably about 20 to about 90 weight percent.

In an alternative embodiment shown in Fig. 3, a tertiary layer 320 of a tertiary coating composition can be applied to at least a portion of the surface, 10 and preferably over the entire surface, of a secondary layer 315, i.e. such a fiber strand 312 would have a primary layer 314 of a primary sizing, a secondary layer 315 of a secondary coating composition and a tertiary, outer layer 320 of the tertiary coating. The tertiary coating is preferably different from the primary sizing composition and the secondary coating composition, 15 i.e. the tertiary coating composition (1) contains at least one component which is chemically different from the components of the primary sizing and secondary coating composition; or (2) contains at least one component in an amount which is different from the amount of the same component contained in the primary sizing or secondary coating composition.

20 In this embodiment, the secondary coating composition comprises one or more polymeric materials discussed above, such as polyurethane, and the tertiary powdered coating composition comprises solid particles, such as the PolarTherm® boron nitride particles, and hollow particles, such as ROPAQUE® pigments, which are discussed above. Preferably, the 25 powdered coating is applied by passing the strand having a liquid secondary coating composition applied thereto through a fluidized bed or spray device to adhere the powder particles to the tacky secondary coating composition. Alternatively, the strands can be assembled into a fabric 810 before the layer 812 of tertiary coating is applied, as shown in Fig. 8. The weight percent of

powdered solid particles adhered to the coated fiber strand 310 can range from about 0.1 to about 30 weight percent of the total weight of the dried strand.

The tertiary powdered coating can also include one or more polymeric 5 materials such as are discussed above, such as acrylic polymers, epoxies, or polyolefins, conventional stabilizers and other modifiers known in the art of such coatings, preferably in dry powder form.

The coated fiber strands 10, 210, 310 discussed above can be used as continuous strand or further processed into diverse products such as chopped 10 strand, twisted strand, roving and/or fabric, such as wovens, nonwovens, knits and mats. In addition, the coated fiber strands used as warp and weft (i.e. fill) strands of a fabric can be non-twisted (also referred to as untwisted or zero twist) or twisted prior to weaving and the fabric can include various combinations of both twisted and non-twisted warp and weft strands.

15 Although the prior discussion is generally directed toward applying the coating composition of the present invention directly on glass fibers after fiber forming and subsequently incorporating the fibers into a fabric, it should be appreciated by those skilled in the art that the present invention also includes an embodiment wherein the coating composition of the 20 present invention is applied to a fabric after it has been manufactured using various techniques well known in the art. Depending on the processing of the fabric, the coating composition of the present invention can be applied either directly to the glass fibers in the fabric or to another coating already on the glass fibers and/or fabric. For example, the glass 25 fibers can be coated with a conventional starch-oil sizing after forming and woven into a fabric. The fabric can then be treated to remove starch-oil sizing prior to applying the coating composition of the present invention. This sizing removal can be accomplished using techniques well known in the art, such as thermal treatment or washing of the fabric. In this

instance, the coating composition would directly coat the surface of the fibers of the fabric. If any portion of the sizing composition initially applied to the glass fibers after forming is not removed, the coating composition of the present invention would then be applied over the remaining portion of 5 the sizing composition rather than directly to the fiber surface.

In another embodiment of the present invention, selected components of the coating composition of the present invention can be applied to the glass fibers immediately after forming and the remaining components of the coating composition can be applied to the fabric after it 10 is made. In a manner similar to that discussed above, some or all of the selected components can be removed from the glass fibers prior to coating the fibers and fabric with the remaining components. As a result, the remaining components will either directly coat the surface of the fibers of the fabric or coat those selected components that were not removed 15 from the fiber surface.

The coated fiber strands 10, 210, 310 and products formed therefrom can be used in a wide variety of applications, but are preferably used as reinforcements 410 for reinforcing polymeric matrix materials 412 to form a composite 414, such as is shown in Fig. 4, which will be discussed in detail 20 below. Such applications include but are not limited to laminates for printed circuit boards, reinforcements for telecommunications cables, and various other composites.

One advantage of the coated strands of the present invention is that they are compatible with typical polymeric matrix resins used to make 25 electronic supports and printed circuit board and are suitable for use on air-jet looms, which are commonly used to make the reinforcing fabrics for such applications. Conventional sizing compositions applied to fibers to be woven using air-jet looms include components (such as starches and oils) that are generally not compatible with such resin systems. It has been observed that

weaving characteristics of fiber strands coated with a residue of a primary sizing composition comprising particles 18 in accordance with the present invention approximate the weaving characteristics of fiber strands coated with conventional starch/oil based sizing compositions and are compatible with

- 5 FR-4 epoxy resins. Although not meant to be bound by any particular theory, it is hypothesized that the particles 18 of the instant invention function in a manner similar to the starch component of conventional starch/oil sizing compositions during processing and air-jet weaving by providing the necessary fiber separation and air drag for the air jet weaving operation while
- 10 further providing compatibility with the epoxy resin system that is not typical of conventional starch/oil sizing compositions. More specifically, the particles 18 contribute a dry, powder characteristic to the coating similar to the dry lubricant characteristics of a starch coating.

Another advantage of the coated strands of the present invention is

- 15 that the particles provide interstices between the fibers of the strand which facilitate flow of the matrix materials therebetween to more quickly and/or uniformly wet-out and wet-through the fibers of the strand. Surprisingly, the amount of particles can exceed 20 weight percent of the total solids of the coating composition applied to the fibers, yet still be adequately adhered to
- 20 the fibers and provide strands having handling characteristics at least comparable to strands without the particle coating.

In another embodiment shown in Fig. 5, coated fiber strands 510 made according to the present invention can be used as warp and/or weft strands 514, 516 in a knit or woven fabric 512 reinforcement, preferably to form a

- 25 laminate for a printed circuit board (shown in Figs. 6-8). Although not required, the warp strands 514 can be twisted prior to use by any conventional twisting technique known to those skilled in the art, for example by using twist frames to impart twist to the strand at about 0.5 to about 3 turns per inch. The reinforcing fabric 512 can include about 5 to about 100 warp

strands 514 per centimeter (about 13 to 254 warp strand per inch) and preferably has about 6 to about 50 weft strands per centimeter (about 15 to about 127 weft strands per inch). The weave construction can be a regular plain weave or mesh (shown in Fig. 5), although any other weaving style well known to those skilled in the art, such as a twill weave or satin weave, can be used.

A suitable woven reinforcing fabric 512 can be formed by using any conventional loom well known to those skilled in the art, such as a shuttle loom, air jet loom or rapier loom, but preferably is formed using an air jet loom (discussed above). Preferred air jet looms are commercially available from Tsudakoma of Japan as Model Nos. 103, 103I 1033 or ZAX; Sulzer Ruti Model Nos. L-5000, L-5100 or L-5200 which are commercially available from Sulzer Brothers LTD. of Zurich, Switzerland; and Toyoda Model No. JAT610.

The fabric of the present invention is preferably woven in a style which is suitable for use in a laminate for an electronic support or printed circuit board, such as are disclosed in "Fabrics Around the World", a technical bulletin of Clark-Schwebel, Inc. of Anderson, South Carolina (1995), which is hereby incorporated by reference. For example, a non-limiting fabric style using E225 E-glass fiber yarns is Style 2116, which has 118 warp yarns and 114 fill (or weft) yarns per 5 centimeters (60 warp yarns and 58 fill yarns per inch); uses 7 22 1x0 (E225 1/0) warp and fill yarns; has a nominal fabric thickness of about 0.094 millimeters (about 0.037 inches); and a fabric weight (or basis weight) of about 103.8 grams per square meter (about 3.06 ounces per square yard). A non-limiting example of a fabric style using G75 E-glass fiber yarns is Style 7628, which has 87 warp yarns and 61 fill yarns per 5 centimeters (44 warp yarns and 31 fill yarns per inch); uses 9 68 1x0 (G75 1/0) warp and fill yarns; has a nominal fabric thickness of about 0.173 millimeters (about 0.0068 inches); and a fabric weight of about 203.4 grams per

square meter (about 6.00 ounces per square yard). A non-limiting example of a fabric style using D450 E-glass fiber yarns is Style 1080, which has 118 warp yarns and 93 fill yarns per 5 centimeters (60 warp yarns and 47 fill yarns per inch); uses 5 11 1x0 (D450 1/0) warp and fill 5 yarns; has a nominal fabric thickness of about 0.053 millimeters (about 0.0021 inches); and a fabric weight of about 46.8 grams per square meter (about 1.38 ounces per square yard). A non-limiting example of a fabric style using D900 E-glass fiber yarns is Style 106, which has 110 warp yarns and 110 fill yarns per 5 centimeters (56 warp yarns and 56 fill 10 yarns per inch); uses 5 5.5 1x0 (D900 1/0) warp and fill yarns; has a nominal fabric thickness of about 0.033 millimeters (about 0.013 inches); and a fabric weight of about 24.4 grams per square meter (about 0.72 ounces per square yard). Another non-limiting example of a fabric style using D900 E-glass fiber yarns is Style 108, which has 118 warp yarns 15 and 93 fill yarns per 5 centimeters (60 warp yarns and 47 fill yarns per inch); uses 5 5.5 1x2 (D900 1/2) warp and fill yarns; has a nominal fabric thickness of about 0.061 millimeters (about 0.0024 inches); and a fabric weight of about 47.5 grams per square meter (about 1.40 ounces per square yard). A non-limiting example of a fabric style using both E225 20 and D450 E-glass fiber yarns is Style 2113, which has 118 warp yarns and 110 fill yarns per 5 centimeters (60 warp yarns and 56 fill yarns per inch); uses 7 22 1x0 (E225 1/0) warp yarn and 5 11 1x0 (D450 1/0) fill yarn; has a nominal fabric thickness of about 0.079 millimeters (about 0.0031 inches); and a fabric weight of about 78.0 grams per square 25 meter (about 2.30 ounces per square yard). A non-limiting example of a fabric style using both G50 and G75 E-glass fiber yarns is Style 7535 which has 87 warp yarns and 57 fill yarns per 5 centimeters (44 warp yarns and 29 fill yarns per inch); uses 9 68 1x0 (G75 1/0) warp yarn and 9 99 1x0 (G50 1/0) fill yarn; has a nominal fabric thickness of about

0.201 millimeters (about 0.0079 inches); and a fabric weight of about 232.3 grams per square meter (about 6.85 ounces per square yard).

These and other useful fabric style specification are given in IPC-EG-140 "Specification for Finished Fabric Woven from 'E' Glass for Printed

- 5 Boards", a publication of The Institute for Interconnecting and Packaging Electronic Circuits (June 1997), which is hereby incorporated by reference. Although the aforementioned fabric styles use twisted yarns, it is contemplated that these or other fabric styles using zero-twist yarns or rovings in conjunction with or in lieu of twisted yarns can be made in
- 10 accordance with the present invention. It is further contemplated that some or all of the warp yarn in the fabric can have fibers coated with a first resin compatible sizing composition and some or all of the fill yarn can have fibers coated with a second resin compatible coating different from the first composition, i.e. the second composition (1) contains at least
- 15 one component which is chemically different from the components of the first sizing composition; or (2) contains at least one component in an amount which is different from the amount of the same component contained in the first sizing composition.

It should be appreciated that the laminates can also be a unidirectional

- 20 laminate wherein most of the fibers, yarns or strands in each layer of fabric are oriented in the same direction.

Referring now to Fig. 6, the fabric 612 can be used to form a composite or laminate 614 by coating and/or impregnating with a polymeric film-forming thermoplastic or thermosetting matrix material 616. The

- 25 composite or laminate 614 is suitable for use as a electronic support. As used herein, "electronic support" means a structure that mechanically supports and/or electrically interconnects elements including but not limited to active electronic components, passive electronic components, printed circuits, integrated circuits, semiconductor devices and other hardware associated

with such elements including but not limited to connectors, sockets, retaining clips and heat sinks.

Matrix materials useful in the present invention include thermosetting materials such as thermosetting polyesters, vinyl esters, epoxides (containing 5 at least one epoxy or oxirane group in the molecule, such as polyglycidyl ethers of polyhydric alcohols or thiols), phenolics, aminoplasts, thermosetting polyurethanes, derivatives and mixtures thereof. Preferred matrix materials for forming laminates for printed circuit boards are FR-4 epoxy resins, polyimides and liquid crystalline polymers, the compositions of which are well 10 known to those skilled in the art. If further information regarding such compositions is needed, see Electronic Materials Handbook™, ASM International (1989) at pages 534-537.

Non-limiting examples of suitable polymeric thermoplastic matrix materials include polyolefins, polyamides, thermoplastic polyurethanes and 15 thermoplastic polyesters, vinyl polymers and mixtures thereof. Further examples of useful thermoplastic materials include polyimides, polyether sulfones, polyphenyl sulfones, polyetherketones, polyphenylene oxides, polyphenylene sulfides, polyacetals, polyvinyl chlorides and polycarbonates.

Other components which can be included with the polymeric matrix 20 material and reinforcing material in the composite include colorants or pigments, lubricants or processing aids, ultraviolet light (UV) stabilizers, antioxidants, other fillers and extenders.

The fabric 612 can be coated and impregnated by dipping the fabric 25 612 in a bath of the polymeric matrix material 616, for example, as discussed in R. Tummala (Ed.), Microelectronics Packaging Handbook, (1989) at pages 895-896, which are hereby incorporated by reference. More generally, chopped or continuous fiber strand reinforcing material can be dispersed in the matrix material by hand or any suitable automated feed or mixing device which distributes the reinforcing material generally evenly throughout the

polymeric matrix material. For example, the reinforcing material can be dispersed in the polymeric matrix material by dry blending all of the components concurrently or sequentially.

The polymeric matrix material 616 and strand can be formed into a

5 composite or laminate 614 by a variety of methods which are dependent upon such factors as the type of polymeric matrix material used. For example, for a thermosetting matrix material, the composite can be formed by compression or injection molding, pultrusion, filament winding, hand lay-up, spray-up or by sheet molding or bulk molding followed by compression or injection molding.

10 Thermosetting polymeric matrix materials can be cured by the inclusion of crosslinkers in the matrix material and/or by the application of heat, for example. Suitable crosslinkers useful to crosslink the polymeric matrix material are discussed above. The temperature and curing time for the thermosetting polymeric matrix material depends upon such factors as the

15 type of polymeric matrix material used, other additives in the matrix system and thickness of the composite, to name a few.

For a thermoplastic matrix material, suitable methods for forming the composite include direct molding or extrusion compounding followed by injection molding. Methods and apparatus for forming the composite by the

20 above methods are discussed in I. Rubin, Handbook of Plastic Materials and Technology (1990) at pages 955-1062, 1179-1215 and 1225-1271, which are hereby incorporated by reference.

In a particular embodiment of the invention shown in Fig. 7, composite or laminate 710 includes fabric 712 impregnated with a compatible matrix

25 material 714. The impregnated fabric can then be squeezed between a set of metering rolls to leave a measured amount of matrix material, and dried to form an electronic support in the form of a semicured substrate or prepreg. An electrically conductive layer 720 can be positioned along a portion of a side 722 of the prepreg in a manner to be discussed below in the

specification, and the prepreg is cured to form an electronic support 718 with an electrically conductive layer. In another embodiment of the invention, and more typically in the electronic support industry, two or more prepgs are combined with one or more electrically conductive layers and laminated

5 together and cured in a manner well known to those skilled in the art, to form a multilayered electronic support. For example, but not limiting the present invention, the prepreg stack can be laminated by pressing the stack, e.g. between polished steel plates, at elevated temperatures and pressures for a predetermined length of time to cure the polymeric matrix and form a laminate

10 of a desired thickness. A portion of one or more of the prepgs can be provided with an electrically conductive layer either prior to or after lamination and curing such that the resulting electronic support is a laminate having at least one electrically conductive layer along a portion of an exposed surface (hereinafter referred to as a "clad laminate").

15 Circuits can then be formed from the electrically conductive layer(s) of the single layer or multilayered electronic support using techniques well known in the art to construct an electronic support in the form of a printed circuit board or printed wiring board (hereinafter collectively referred to as "electronic circuit boards"). If desired, apertures or holes (also referred to as

20 "vias") can be formed in the electronic supports, to allow for electrical interconnection between circuits and/or components on opposing surfaces of the electronic support, by any convenient manner known in the art, including but not limited to mechanical drilling and laser drilling. More specifically, after formation of the apertures, a layer of electrically conductive material is

25 deposited on the walls of the aperture or the aperture is filled with an electrically conductive material to facilitate the required electrical interconnection and/or heat dissipation.

The electrically conductive layer 720 can be formed by any method well known to those skilled in the art. For example but not limiting the present

invention, the electrically conductive layer can be formed by laminating a thin sheet or foil of metallic material onto at least a portion of a side of the semi-cured or cured prepreg or laminate. As an alternative, the electrically conductive layer can be formed by depositing a layer of metallic material onto

5 at least a portion of a side of the semi-cured or cured prepreg or laminate using well known techniques including but not limited to electrolytic plating, electroless plating or sputtering. Metallic materials suitable for use as an electrically conductive layer include but are not limited to copper (which is preferred), silver, aluminum, gold, tin, tin-lead alloys, palladium and

10 combinations thereof.

In another embodiment of the present invention, the electronic support can be in the form of a multilayered electronic circuit board constructed by laminating together one or more electronic circuit boards (described above) with one or more clad laminates (described above) and/or one or more

15 prepregs (described above). If desired, additional electrically conductive layers can be incorporated into the electronic support, for example along a portion of an exposed side of the multilayered electronic circuit board. Furthermore, if required, additional circuits can be formed from the electrically conductive layers in a manner discussed above. It should be appreciated that

20 depending on the relative positions of the layers of the multilayered electronic circuit board, the board can have both internal and external circuits. Additional apertures are formed, as discussed earlier, partially through or completely through the board to allow electrical interconnection between the layers at selected locations. It should be appreciated that the resulting

25 structure can have some apertures that extend completely through the structure, some apertures that extend only partially through the structure, and some apertures that are completely within the structure.

The instant invention further contemplates the fabrication of multilayered laminates and electronic circuit boards which include at least one

composite layer made according to the teachings herein and at least one composite layer made in a manner different from the composite layer taught herein, e.g. made using conventional glass fiber composite technology. More specifically and as is well known to those skilled in the art, traditionally the

5 filaments in continuous glass fiber strands used in weaving fabric are treated with a starch/oil sizing which includes partially or fully dextrinized starch or amylose, hydrogenated vegetable oil, a cationic wetting agent, emulsifying agent and water, including but not limited to those disclosed in Loewenstein at pages 237-244 (3d Ed. 1993), which is hereby incorporated by reference.

10 Warp yarns produced from these strands are thereafter treated with a solution prior to weaving to protect the strands against abrasion during the weaving process, e.g. poly(vinyl alcohol) as disclosed in U.S. Patent No. 4,530,876 at column 3, line 67 through column 4, line 11, which is hereby incorporated by reference. This operation is commonly referred to as slashing. The poly(vinyl

15 alcohol) as well as the starch/oil size are generally not compatible with the polymeric matrix material used by composite manufacturers and the fabric must be cleaned to remove essentially all organic material from the surface of the glass fibers prior to impregnating the woven fabric. This can be accomplished in a variety ways, for example by scrubbing the fabric or, more

20 commonly, by heat treating the fabric in a manner well known in the art. As a result of the cleaning operation, there is no suitable interface between the polymeric matrix material used to impregnate the fabric and the cleaned glass fiber surface, so that a coupling agent must be applied to the glass fiber surface. This operation is sometime referred to by those skilled in the art as

25 finishing. The coupling agents most commonly used in finishing operations are silanes, including but not limited to those disclosed in E. P. Plueddemann, Silane Coupling Agents (1982) at pages 146-147, which is hereby incorporated by reference. Also see Loewenstein at pages 249-256 (3d Ed. 1993). After treatment with the silane, the fabric is impregnated with a

compatible polymeric matrix material, squeezed between a set of metering rolls and dried to form a semicured prepreg as discussed above. It should be appreciated that depending on the nature of the sizing, the cleaning operation and/or the matrix resin used in the composite, the slashing and/or finishing

5 steps can be eliminated. One or more prepgres incorporating conventional glass fiber composite technology can then be combined with one or more prepgres incorporating the instant invention to form an electronic support as discussed above, and in particular a multilayered laminate or electronic circuit board. For more information regarding fabrication of electronic circuit boards,

10 see Electronic Materials Handbook™, ASM International (1989) at pages 113-115, R. Tummala (Ed.), Microelectronics Packaging Handbook, (1989) at pages 858-861 and 895-909, M. W. Jawitz, Printed Circuit Board Handbook (1997) at pages 9.1-9.42, and C. F. Coombs, Jr. (Ed.), Printed Circuits Handbook, (3d Ed. 1988), pages 6.1-6.7, which are hereby incorporated by

15 reference.

The composites and laminates forming the electronic supports of the instant invention can be used to form packaging used in the electronics industry, and more particularly first, second and/or third level packaging, such as that disclosed in Tummala at pages 25-43, which is hereby incorporated by reference. In addition, the present invention can also be used for other packaging levels.

The present invention also includes a method for reinforcing a polymeric matrix material to form a composite. The method comprises:

(1) applying to a glass fiber strand reinforcing material the above primary

25 sizing, secondary coating and/or tertiary coating composition including particles which provide interstitial spaces between adjacent glass fibers of the strand, (2) drying the coating to form a substantially uniform coating upon the reinforcing material; (3) combining the reinforcing material with the polymeric matrix material; and (4) at least partially curing the polymeric matrix material

to provide a reinforced polymeric composite in a manner such as is discussed in detail above. Although not limiting the present invention, the reinforcing material can be combined with the polymeric matrix material, for example by dispersing it in the matrix material.

5 The present invention also includes a method for inhibiting adhesion between adjacent glass fibers of a glass fiber strand, comprising the steps of: (1) applying to a glass fiber strand the above primary sizing, secondary coating or tertiary coating composition including particles which provide interstitial spaces between adjacent glass fibers of the strand; (2) drying the
10 coating to form a substantially uniform coating upon the glass fibers of the glass fiber strand, such that adhesion between adjacent glass fibers of the strand is inhibited.

The present invention will now be illustrated by the following specific, non-limiting examples.

15

EXAMPLE 1

Each of the components in the amounts set forth in Table 1 were mixed to form aqueous primary size compositions A, B and C according to the present invention. Each aqueous primary sizing composition was prepared in
20 a similar manner to that discussed above. Less than about 1 weight percent of acetic acid on a total weight basis was included in each composition. Each of the aqueous sizing compositions of Table 1 was coated onto fibers forming G-75 E-glass fiber strands.

Each of the coated glass fiber strands was dried, twisted to form yarn,
25 and wound onto bobbins in a similar manner using conventional twisting equipment. The yarns coated with the sizing compositions exhibited minimal sizing shedding during twisting.

Table 1

COMPONENT	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS		
	Sample		
	A	B	C
Polyvinyl pyrrolidone ²⁹	14.7	14.7	13.4
Cetyl Palmitate ³⁰	30.0	29.9	27.3
Epoxy-functional organo silane coupling agent ³¹	1.8	1.8	1.6
Acrylic-functional organo- silane coupling agent ³²	3.7	3.7	3.3
Softening Agent ³³	2.4	2.4	
Emulsifying Agent ³⁴	1.6	1.6	1.5
Emulsifying Agent ³⁵	3.3	3.3	3.0
Antifoaming Agent ³⁶	0.2	0.2	0.2
Styrene/Acrylic Copolymer Hollow Particle Dispersion ³⁷	0	42.4	0
Styrene/Acrylic Copolymer Hollow Particle Dispersion ³⁸	42.3	0	38.6
Boron Nitride Dispersion ³⁹	0	0	6.3
Boron Nitride Powder ⁴⁰	0	0	2.6

²⁹ PVP K-30 polyvinyl pyrrolidone which is commercially available from ISP Chemicals of Wayne, NJ.

³⁰ STEPANTEX 653 which is commercially available from Stepan Company of Maywood, NJ

³¹ A-187 gamma-glycidoxypropyltrimethoxysilane which is commercially available from OSi Specialties, Inc. of Tarrytown, NY.

³² A-174 gamma-methacryloxypropyltrimethoxysilane which is commercially available from OSi Specialties, Inc. of Tarrytown, NY.

³³ EMERY® 6717 partially amidated polyethylene imine which is commercially available from Henkel Corporation of Kankakee, IL.

³⁴ MACOL OP-10 ethoxylated alkylphenol which is commercially available from BASF Corp. of Parsippany, NJ.

³⁵ TMAZ-81 ethylene oxide derivative of a sorbitol ester which is commercially available from BASF Corp. of Parsippany, NJ.

³⁶ MAZU DF-136 antifoaming agent which is commercially available from BASF Corp. of Parsippany, NJ.

³⁷ ROPAQUE® HP-1055, 1.0 micron particle dispersion which is commercially available from Rohm and Haas Company of Philadelphia, PA.

³⁸ ROPAQUE® OP-96, 0.55 micron particle dispersion which is commercially available from Rohm and Haas Company of Philadelphia, PA.

³⁹ ORPAC BORON NITRIDE RELEASECOAT-CONC boron nitride dispersion which is commercially available from ZYP Coatings, Inc. of Oak Ridge, TN.

Yarns sized with the each of the sizing compositions (A, B and C) were used as fill yarn in weaving a 7628 style fabric using a Sulzer Ruti Model 5200 air-jet loom. The warp yarn was a twisted G-75 E-glass fiber strand with 5 fiber coated with a different resin compatible sizing composition⁴¹. The fabrics were subsequently pre-pregged with an FR-4 epoxy resin having a Tg of about 140°C (designated 4000-2 resin by Nelco International Corporation of Anaheim, CA). The sizing compositions were not removed from the fabric prior to pre-pregging. Laminates were made by stacking 8-plies of the pre- 10 prepped material between two layers of 1 ounce copper and laminating them together at a temperature of about 355°F (about 179°C), pressure of about 300 pounds per square inch (about 2.1 megaPascals) for about 150 minutes (total cycle time). The thickness of the laminates without copper ranged from about 0.043 inches (about 0.11 centimeters) to about 0.050 inches (0.13 15 centimeters).

After forming, the laminates (designated A, B and C according to the fiber strands from which they were made) were tested as indicated below in Table 2. During testing, laminate B tested at the same time as a first laminate made from glass fiber yarn coated with sizing composition Sample A 20 (hereinafter designated as Laminate Sample A1). At a later date, laminate C was tested at the same time as a second laminate made from glass fiber yarn coated with sizing composition Sample C (hereinafter designated as Laminate Sample A2).

⁴⁰ PolarTherm® PT 160 boron nitride powder which is commercially available from Advanced Ceramics Corporation of Lakewood, OH.

⁴¹ The warp yarn was PPG Industries, Inc.'s commercially available fiber glass yarn product designated as G-75 glass fiber yarn coated with PPG Industries, Inc.'s 1383 binder.

Table 2

Test	Units	Laminate Sample			
		A1*	B*	A2**	C**
Average Thickness	inches	0.048	0.048	0.053-0.055	0.053-0.055
Solder Float	seconds	409	386	235	253
Solder Dip	seconds	320	203	243	242
Flexural Strength Warp Direction ⁴²	kpsi	99	102	91	90
Flexural Strength Weft Direction ⁴³	kpsi	86	81	73	72

* based on 2 samples

** based on 3 samples

The solder float test was conducted by floating an 4 inch by 4 inch square (10.16 centimeters by 10.16 centimeters) of the copper clad laminate in a eutectic lead-tin solder bath at about 550°F (about 288°C) until blistering or delamination was observed. The time until the first blister or delamination was then recorded in seconds.

The solder dip test was conducted by cutting a sample of the laminate, removing the copper from the sample by etching, smoothing the cut edges of the sample by polishing and placing the sample in a pressure cooker at 250°F (about 121°C) and 15 pounds per square inch (about 0.1 megaPascals) for about 60 minutes. After the 60 minute exposure, the sample was removed from the pressure cooker, patted dry and dipped into a eutectic lead-tin solder bath at about 550°F (about 288°C) until blistering or delamination was observed. The time until the first blister or delamination was then recorded in seconds.

The flexural testing was conducted according to the IPC standard indicated.

⁴² Per IPC-TM-650 "Flexural Strength of Laminates (At Ambient Temperature)", 12/94, Revision B.

⁴³ Ibid.

The laminates A, B and C made using fiber strands sized with sizing compositions A, B and C respectively, had acceptable properties (shown in Table 2) for use as electronic supports for printed circuit boards.

5

EXAMPLE 2

Each of the components in the amounts set forth in Table 3 were mixed to form aqueous size composition Samples D, E and F according to the present invention. Less than about 0.5 weight percent of acetic acid on a total weight basis was included in each composition.

10

Table 3

COMPONENT	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS		
	D	E	F
polyvinyl pyrrolidone ⁴⁴	12.3	11.7	12.3
cetyl palmitate ⁴⁵	25.0	23.9	25.0
emulsifying agent ⁴⁶	3.5	3.9	2.7
emulsifying agent ⁴⁷	1.8	2.0	1.4
boron nitride powder particles ⁴⁸	2.4	2.3	2.4
cationic lubricant ⁴⁹	2.0	2.0	2.0
acrylic-functional organo-silane coupling agent ⁵⁰	3.1	2.9	3.1
epoxy-functional organo-silane	1.5	1.4	1.5

⁴⁴ PVP K-30 polyvinyl pyrrolidone which is commercially available from ISP Chemicals of Wayne, NJ.

⁴⁵ STEPANTEX 653 cetyl palmitate which is commercially available from Stepan Company of Chicago, IL.

⁴⁶ TMAZ 81 ethylene oxide derivative of a sorbitol ester which is commercially available BASF of Parsippany, New Jersey.

⁴⁷ MACOL OP-10 ethoxylated alkylphenol, which is commercially available from BASF of Parsippany, New Jersey

⁴⁸ PolarTherm® PT 160 boron nitride powder particles, which are commercially available from Advanced Ceramics Corporation of Lakewood, OH.

⁴⁹ EMERY® 6717 partially amidated polyethylene imine which is commercially available from Henkel Corporation of Kankakee, IL.

⁵⁰ A-174 gamma-methacryloxypropyltrimethoxysilane which is commercially available from OSI Specialties, Inc. of Tarrytown, NY.

coupling agent ⁵¹			
boron nitride particles in aqueous suspension ⁵²	5.7	5.5	5.6
antifoaming agent ⁵³	0.2	0.2	0.2
styrene/ acrylic copolymer hollow particle dispersion ⁵⁴	35.2	33.7	35.3
epoxidized linseed oil ⁵⁵	7.3	10.5	0
epoxidized soybean oil ⁵⁶	0	0	7.3
weight percent solids	3.4	3.5	3.4
LOI	0.42	0.39	0.30

Each of the aqueous size compositions of Table 3 were used to coat glass fibers forming G-75 E-glass fiber strands. Each coated glass fiber strand was dried, twisted to form a yarn, and wound onto bobbins in a similar manner using conventional twisting equipment.

The yarn of Sample D was evaluated by comparing the coated yarn to yarn coated with a sizing composition similar to Sample D but without the epoxidized linseed oil (hereinafter "Comparative Sample 1"). This comparison included visual inspection of the appearance of a 7628 style fabric woven on an air jet loom. The woven fabric used Sample D as the fill yarn a twisted G-75 E-glass fiber strand with fiber coated with a different resin compatible sizing composition⁵⁷ as the warp yarn. It was observed that fabric woven with yarn coated with Sample D exhibited less loose fuzz on

⁵¹ A-187 gamma-glycidoxypropyltrimethoxysilane which is commercially available from OSI Specialties, Inc. of Tarrytown, NY.

⁵² ORPAC BORON NITRIDE RELEASECOAT-CONC boron nitride dispersion which is dispersion of about 25 weight percent boron nitride particles in water commercially available from ZYP Coatings, Inc. of Oak Ridge, TN.

⁵³ MAZU DF-136 antifoaming agent which is commercially available from BASF Company of Parsippany, New Jersey.

⁵⁴ ROPAQUE® OP-96, 0.55 micron particle dispersion which is commercially available from Rohm and Haas Company of Philadelphia, PA.

⁵⁵ FLEXOL LOE epoxidized linseed oil commercially available from Union Carbide of Danbury, Connecticut.

⁵⁶ FLEXOL EPO epoxidized soybean oil commercially available from Union Carbide of Danbury, Connecticut.

⁵⁷ The warp yarn was PPG Industries, Inc.'s commercially available fiber glass yarn product designated as G-75 glass fiber yarn coated with PPG Industries, Inc.'s 1383 binder.

the fabric as well as less collected fuzz at contact points on the loom, especially at the yarn accumulator, when compared to fabric woven with yarn coated with Comparative Sample 1. No fabric was woven using yarn incorporating fibers coated with Samples E or F because of the high initial 5 amount of fuzz observed on the loom. It is believed that this condition was the result of an LOI level lower than required to prevent excess fuzz formation. In the present invention, it is anticipated that an LOI of at least 0.40 for the sizing compositions discussed above is required to reduce fuzz formation during weaving.

10

EXAMPLE 3

The yarns of Samples A, B and C and a Comparative Sample 2⁵⁸ (yarn coated with a starch/oil sizing) were evaluated for several physical properties, such as loss on ignition (LOI), air jet compatibility (Air Drag) and Friction 15 Force. The results are shown in Table 4.

The loss on ignition (weight percent of solids of the forming size composition divided by the total weight of the glass and dried forming size composition) of each Sample is set forth in Table 4.

Each yarn was evaluated for Air Drag Force or tension by feeding the 20 yarn at a controlled feed rate of 274 meters (300 yards) per minute through a checkline tension meter, which applied a tension to the yarn, and a Ruti two millimeter diameter air nozzle at an air pressure of 138 kPa (20 pounds per square inch).

The Samples and Comparative Sample 2 were also evaluated for 25 Friction Force by applying a tension of about 20 grams to each yarn sample as the sample is pulled at a rate of 274 meters (300 yards) per minute through a pair of conventional tension measurement devices having a

⁵⁸ The yarn was PPG Industries, Inc.'s commercially available fiber glass yarn designated as G-75 glass fiber yarn coated with PPG Industries, Inc.'s 695 starch/oil binder.

stationary chrome post of about 5 centimeters (2 inches) diameter mounted therebetween to displace the yarn about 5 centimeters from a straight line path between the tension measurement devices. The difference in force in grams is set forth in Table 7 below. The Friction Force test is intended to

5 simulate the frictional forces to which the yarn is subjected during weaving operations.

During testing, Samples B and 2 were tested at the same time as a first quantity of glass fiber yarn coated with sizing composition Sample A (hereinafter designated as Sample A3) and Sample C was tested at the 10 same time as a second quantity of glass fiber yarn coated with sizing composition Sample A (hereinafter designated as Sample A4). Samples A3, A4 and B were about 2.8 weight percent solids. Sample C was about 3.1 weight percent solid. Comparative Sample 2 was about 5.9 weight percent solid.

15

Table 4

	Sample				
	A3	B	2	A4	C
LOI (weight percent)	0.42	0.49	1.11	0.38	0.37
Air Drag (grams)	56.2	51.2	52.9	58.8	53.2
Friction force (grams)	53.6	61.5	95.1	48.8	68.9

From Table 4, it can be seen that sizing Samples A, B and C have an air drag comparable to that of Comparative Sample 2 (starch/oil binder).

20 Furthermore, the lower friction force in Samples A, B and C indicates that the yarn is more easily removed from the loom accumulator during weaving when compared to Comparative Sample 1.

EXAMPLE 4

The yarns of Samples A, B and C and Comparative Sample 2 were evaluated for Air Drag in a similar manner to Example 3 above, except that the Air Drag values were determined for a bobbin sample at the pressures 5 indicated in Table 5. Each yarn also was evaluated for average number of broken filaments per 1200 meters of yarn at 200 meters per minute using a Shirley Model No. 84 041L broken filament detector, which is commercially available from SDL International Inc. of England (shown in Table 5 as Test 1). The broken filament values are reported from sections taken from a full 10 bobbin, the same bobbin after removing 227 grams (0.5 pounds) and the same bobbin after removing 4540 grams (10 pounds) of yarn. Each yarn was further evaluated for the number of broken filaments at increasing levels of tension and abrasion (shown in Table 5 as Test 2). In Test 2, a sample of yarn was unwound from a bobbin at 200 meters/minute, threaded in a 15 serpentine manner through a series of 8 ceramic pins on a uniform tension control device (sometimes referred to as a gate tensioning device), and passed through the Shirley broken filament detector (discussed above) to count the number of broken filaments. The spacing of the pins on the tensioning device was varied using different dial settings to provide various 20 levels of tension in the yarn. This particular test used a Model UTC-2003 tensioning device commercially available from Steel Heddle Co. of South Carolina. The broken filaments were reported in number of broken filaments per meter of yarn.

The results of these tests for Samples A, B and C and Comparative 25 Sample 2 are set forth in Table 5 below. In a manner similar to that discussed above in Example 3, Samples B and 2 were tested at the same time as a first quantity of glass fiber yarn coated with sizing composition Sample A (hereinafter designated as Sample A5) and at a latter date Sample

C was tested at the same time as a second quantity of glass fiber yarn coated with sizing composition Sample A (hereinafter designated as Sample A6).

TABLE 5

	Sample				
	A5	B	2	A6	C
AIR DRAG (grams)					
15 psi	46.10	42.50	42.23	47.47	42.33
20 psi	56.20	51.20	52.94	58.84	53.18
25 psi	67.33	60.30	64.13	69.45	67.66
30 psi	77.34	70.84	75.74	75.29	77.63
35 psi	89.42	89.96	85.96	83.70	82.74
40 psi	104.97	101.21	98.48	87.23	92.18
45 psi	113.41	107.74	110.34	99.91	102.91
TEST 1					
full bobbin	0.170	0.882	0.032	1.735	0.066
227 grams (0.5 pound)	0.160	0.648	0.041	0.904	0.075
4540 grams (10 pounds)	0.098	1.348	0.008	0.518	0.022
TEST 2					
Setting 2	0.683	5.017	0.119	0.372	0.011
Setting 3	0.753	4.772	0.083	0.450	0.017
Setting 4	0.713	3.753	0.147	0.367	0.017
Setting 5	1.267	4.025	0.150	0.811	0.061
Setting 6	1.608	8.383	0.322	0.286	0.044
Setting 7	4.128	6.517	0.611	0.403	0.058
Setting 8	4.472	14.800	0.978	0.406	0.128

5

As can be seen in Table 5, sizing Samples A, B and C have an air drag comparable to that of Comparative Sample 2 (starch/oil binder).

From the foregoing description, it can be seen that the present

10 invention provides glass fiber strands having an abrasion-resistant coating which provide good thermal stability, low corrosion and reactivity in the presence of high humidity, reactive acids and alkalies and compatibility with a

variety of polymeric matrix materials. These strands can be twisted or chopped, formed into a roving, chopped mat or continuous strand mat or woven or knitted into a fabric for use in a wide variety of applications, such as reinforcements for composites such as printed circuit boards.

5 It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications that are within the spirit and scope of the invention, as defined
10 by the appended claims.

WE CLAIM:

1. A coated fiber strand comprising at least one fiber having a layer of a dried residue of a resin compatible coating composition on at least a portion of a surface of the at least one fiber, the resin compatible coating composition comprising:
 - (a) a plurality of discrete, dimensionally stable particles formed from materials selected from the group consisting of organic materials, polymeric materials, composite materials and mixtures thereof
 - 10 that provide an interstitial space between the at least one fiber and at least one adjacent fiber, the particles having an average particle size of about 0.1 to about 5 micrometers;
 - (b) at least one lubricious material;
 - (c) at least one polymeric film former; and
 - 15 (d) at least one coupling agent.
2. The fiber strand according to claim 1, wherein the at least one fiber is an inorganic fiber formed from a glass material selected from the group consisting of E-glass, D-glass, S-glass, Q-glass, E-glass derivatives and combinations thereof.
3. The fiber strand according to claim 1, wherein the resin compatible coating composition is a resin compatible primary sizing composition that is compatible with an epoxy resin.
- 25 4. The fiber strand according to claim 1, wherein the particles have a Mohs' hardness value of less than that of the at least one fiber.

- 70 -

5. The fiber strand according to claim 4, wherein the particles have a Mohs' hardness value of less than about 6.

6. The fiber strand according to claim 1, wherein the resin
5 compatible coating composition is a secondary coating composition.

7. The fiber strand according to claim 1, wherein the particles have an average particle size of about 0.5 to about 2 micrometers.

10 8. The fiber strand according to claim 1, wherein the particles comprise from about 20 to about 60 weight percent of the resin compatible coating composition on a total solids basis.

9. The fiber strand according to claim 8, wherein the particles
15 comprise from about 35 to about 55 weight percent of the resin compatible coating composition on a total solids basis.

10. The fiber strand according to claim 1, wherein at least one of the particles comprises a hollow particle.

20

11. The fiber strand according to claim 10, wherein the hollow particle is formed from a copolymer of styrene and acrylic.

12. The fiber strand according to claim 1, wherein at least one of
25 the particles comprises a polymeric material selected from the group consisting of inorganic polymeric materials, synthetic organic polymeric materials, semisynthetic organic polymeric materials and natural organic polymeric materials.

13. The fiber strand according to claim 12, wherein the at least one particle comprises an organic polymeric material selected from the group consisting of thermosetting polymeric materials and thermoplastic polymeric materials.

5

14. The fiber strand according to claim 13, wherein the at least one particle comprises a thermoplastic polymeric material selected from the group consisting of acrylic polymers, vinyl polymers, thermoplastic polyesters, polyolefins, polyamides, thermoplastic polyurethanes and 10 mixtures thereof.

15. The fiber strand according to claim 14, wherein the at least one particle is formed from an acrylic copolymer which is a copolymer of styrene and acrylic.

15

16. The fiber stand according to claim 13, wherein the at least one particle comprises a thermosetting polymeric material selected from the group consisting of thermosetting polyesters, vinyl esters, epoxy materials, phenolics, aminoplasts, thermosetting polyurethanes and 20 mixtures thereof.

17. The fiber strand according to claim 1, wherein the lubricious material is selected from the group consisting of oils, waxes, greases and mixture thereof.

25

18. The fiber strand according to claim 17, wherein the lubricious material is a wax selected from the group consisting of natural waxes, synthetic waxes and semisynthetic waxes.

19. The fiber strand according to claim 18, wherein the wax is a synthetic wax selected from the group consisting of cetyl palmitate, cetyl laurate, octadecyl laurate, octadecyl myristate, octadecyl palmitate, octadecyl stearate and paraffin.

5

20. The fiber strand according to claim 1, wherein the lubricious material comprises from about 20 to about 40 weight percent of the resin compatible coating composition on a total solids basis.

10

21. The fiber strand according to claim 1, wherein the resin compatible coating composition is essentially free of starch materials.

15

22. The fiber strand according to claim 1, wherein the particles are first particles and the resin compatible coating composition further comprises a plurality of additional discrete, dimensionally stable particles different from the first particles.

20

23. The fiber strand according to claim 22, wherein the plurality of additional particles is formed from an inorganic material selected from the group consisting of metals, graphite, oxides, carbides, nitrides, borides, sulfides, silicates and carbonates.

25

24. The fiber strand according to claim 22, wherein the plurality of additional particles is formed from an inorganic solid lubricant material selected from the group consisting of boron nitride, graphite and metal dichalcogenides.

25. The fiber strand according to claim 1, wherein the polymeric film-forming material comprises a material selected from the group

consisting of thermosetting polymeric materials, thermoplastic polymeric materials, natural polymeric materials and mixtures thereof.

26. The fiber strand according to claim 25, wherein the
5 polymeric film-forming material comprises a thermoplastic polymeric material selected from the group consisting of polyvinyl pyrrolidone, polyvinyl alcohol, polyacrylamide, polyacrylic acid and copolymers and mixtures thereof.

10 27. The fiber strand according to claim 25, wherein the polymeric film-forming material is a thermosetting polymeric material which is selected from the group consisting of epoxy materials, polyesters, polyurethanes and polyacrylates.

15 28. The fiber strand according to claim 25, wherein the polymeric film-forming material comprises about 5 to about 30 weight percent of the resin compatible coating composition on a total solids basis.

20 29. The fiber strand according to claim 1, wherein the particles are non-waxy particles.

30. The fiber strand according to claim 1, wherein the fiber strand is a twisted fiber strand.

25

31. The fiber strand according to claim 1, wherein the fiber strands is a non-twisted fiber strand.

32. The fiber strand according to claim 1, wherein the at least one fiber is a glass fiber manufactured using a direct melt glass fiber forming process.

5 33. The fiber strand according to claim 1, wherein the at least one fiber is a glass fiber manufactured using a marble melting glass fiber forming process.

10 34. The fiber strand according to claim 1, wherein the resin compatible coating composition further comprises a resin reactive diluent.

15 35. The fiber strand according to claim 34, wherein the resin reactive diluent is a lubricant comprising one or more functional groups capable of reacting with an epoxy resin system and selected from the group consisting of amine groups, alcohol groups, anhydride groups, acid groups and epoxy groups.

20 36. A fabric incorporating at least one fiber strand according to claim 1.

37. A fabric incorporating at least one fiber strand according to claim 15.

25 38. A fabric incorporating at least one fiber strand according to claim 24.

39. A fabric incorporating at least one fiber strand according to claim 26.

40. A coated fiber strand comprising at least one glass fiber having a dried residue of an aqueous resin compatible coating composition on at least a portion of a surface of the at least one fiber, the aqueous resin compatible coating composition comprising (a) a plurality of discrete, 5 polymeric organic particles that provide an interstitial space between the at least one glass fiber and at least one adjacent glass fiber, the particles having an average particle size of up to about 5 micrometers, (b) a lubricious material selected from the group consisting of oils, waxes, greases and mixtures thereof, (c) polymeric film-forming material selected 10 from the group consisting of thermosetting polymeric materials, thermoplastic polymeric materials, natural polymeric materials and mixtures thereof, and (d) a coupling agent.

41. The fiber strand according to claim 40, wherein the plurality 15 of particles comprises a plurality of hollow particles comprising material selected from the group consisting of inorganic materials, organic materials, polymeric materials, composite materials and mixtures thereof.

42. The fiber strand according to claim 41, wherein at least one 20 of the plurality of hollow particles is formed from a polymeric materials which is a copolymer of styrene and acrylic.

43. The fiber strand according to claim 42, wherein particles are 25 first particles and the coating composition further comprises a plurality of additional particles comprising an inorganic lubricant material selected from the group consisting of boron nitride, graphite and metal dichalcogenides.

44. A fabric incorporating at least one fiber strand according to claim 40.

45. A coated fiber strand comprising at least one glass fiber 5 having a dried residue of an aqueous resin compatible coating composition on at least a portion of a surface of the at least one fiber, the aqueous resin compatible coating composition comprising:

- (a) a plurality of particles comprising:
 - (i) at least one particle formed from an acrylic copolymer which is a copolymer of styrene and acrylic; and
 - (ii) at least one particle formed from an inorganic solid lubricant material selected from the group consisting of boron nitride, graphite and metal dichalcogenides,
- 10 wherein the particles have an average particle size of up to about 5 micrometers and comprise about 35 to about 55 weight percent of the resin compatible coating composition on a total solids basis;
- 15 (b) a lubricious material selected from the group consisting of cetyl palmitate, cetyl laurate, octadecyl laurate, octadecyl myristate, octadecyl palmitate, octadecyl stearate and paraffin, 20 wherein the lubricious material comprises from about 20 to about 40 weight percent of the resin compatible coating composition on a total solids basis;
- 25 (c) thermoplastic polymeric film forming material selected from the group consisting of polyvinyl pyrrolidone, polyvinyl alcohol, polyacrylamide, polyacrylic acid and copolymers and mixtures thereof, wherein the thermoplastic polymeric film-forming material comprises about 5 to about 30 weight percent of the resin compatible coating composition on a total solids basis; and
- (d) a coupling agent.

46. A fabric incorporating at least one fiber strand according to claim 45.

5 47. A fabric comprising a plurality of fibers strands comprising at least one fiber, at least a portion of the fabric having a residue of a resin compatible coating composition comprising:

10 (a) a plurality of discrete, dimensionally stable particles formed from materials selected from the group consisting of organic materials, polymeric materials, composite materials and mixtures thereof that provide an interstitial space between the at least one fiber and at least one adjacent fiber, the particles having an average particle size of about 0.1 to about 5 micrometers;

15 (b) at least one lubricious material;

(c) at least one polymeric film former; and

(d) at least one coupling agent.

48. The fabric according to claim 47 wherein at least a portion of the fabric comprises twisted glass fiber strand.

20

49. The fabric according to claim 47 wherein at least a portion of the fabric comprises non-twisted glass strand.

50. The fabric according to claim 47 wherein the at least one fiber is 25 a glass fiber manufactured using a direct melt glass fiber forming process.

51. The fabric according to claim 47 wherein the least one fiber is a glass fiber manufactured using a marble melting glass fiber forming process.

52. The fabric according to claim 47 wherein the fabric is a non-woven fabric.

53. The fabric according to claim 47 wherein the fabric is a woven 5 fabric.

54. The fabric according to claim 47 wherein the fabric is woven on an air jet loom.

10 55. The fabric according to claim 54 wherein the at least one fiber is a glass fiber manufactured using a direct melt glass fiber forming process and at least a portion of the fabric comprises twisted glass fiber strand.

15 56. The fabric according to claim 53 wherein the fabric is woven on a rapier loom.

57. The fabric according to claim 56 wherein the at least one fiber is a glass fiber manufactured using a direct melt glass fiber forming process and at least a portion of the fabric comprises twisted glass fiber strand.

20 58. The fabric according to claim 56 wherein the at least one fiber is a glass fiber manufactured using a marble melt glass fiber forming process and at least a portion of the fabric comprises non-twisted glass strand.

25 59. The fabric according to claim 47 wherein the fabric is selected from the group consisting of woven fabrics, nonwoven fabrics and knitted fabrics.

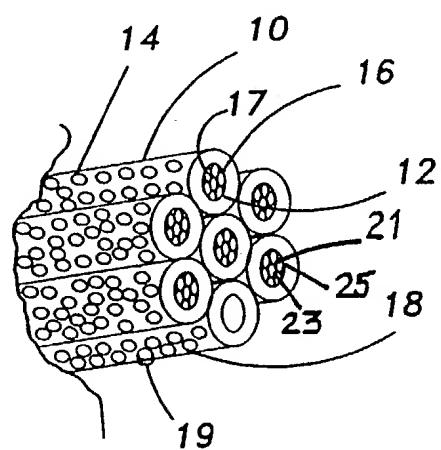


FIG. 1

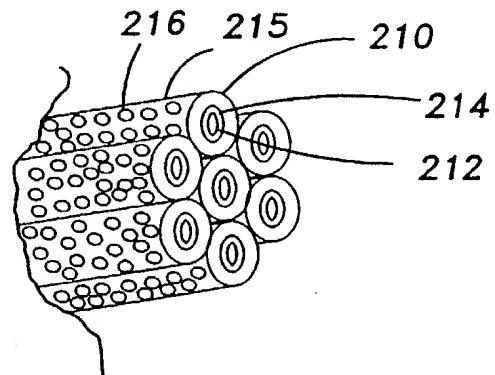


FIG. 2

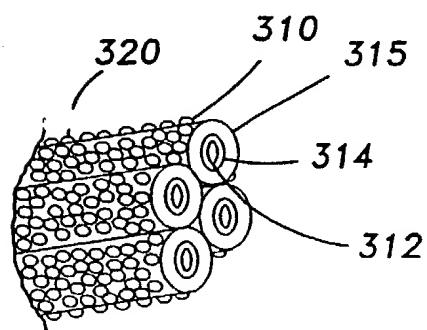


FIG. 3

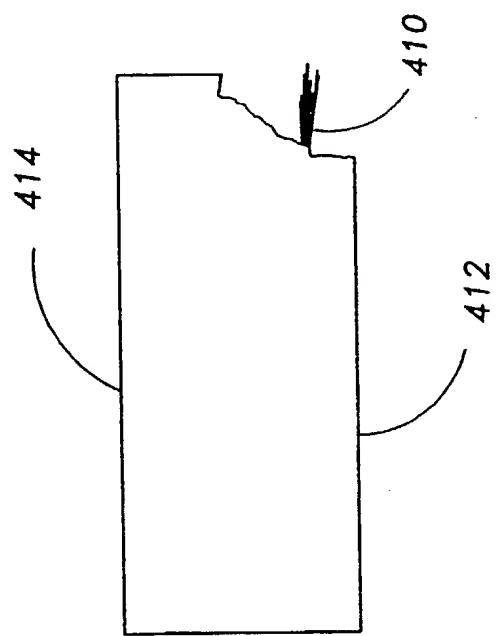


FIG. 4

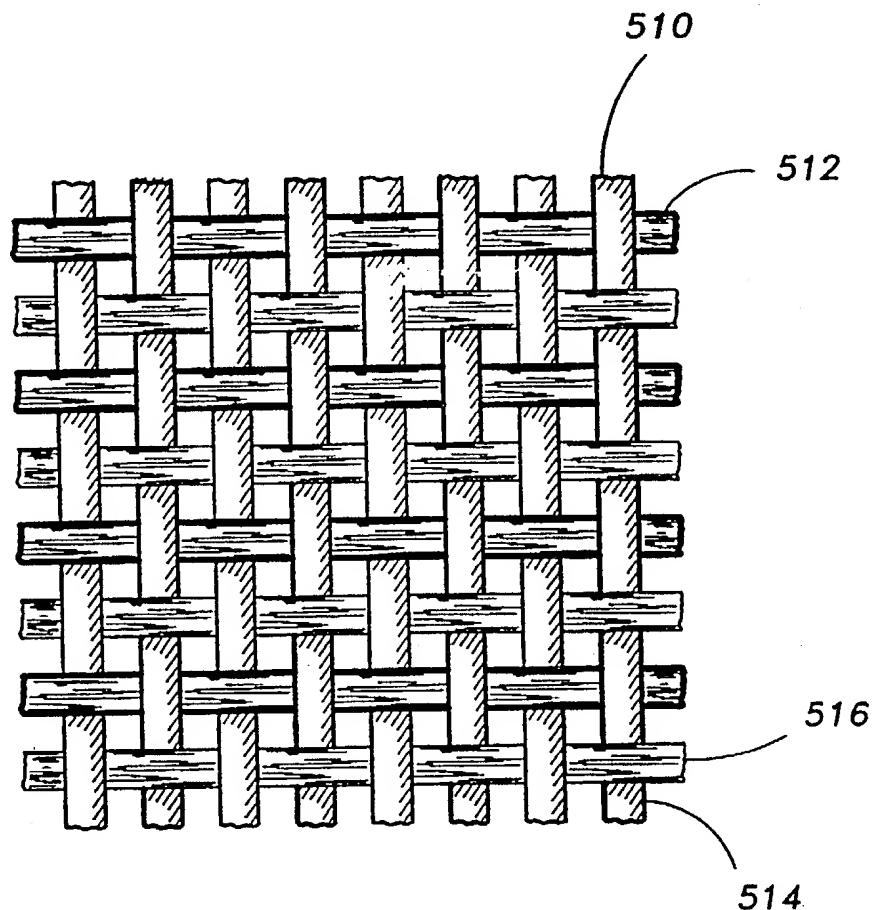


FIG. 5

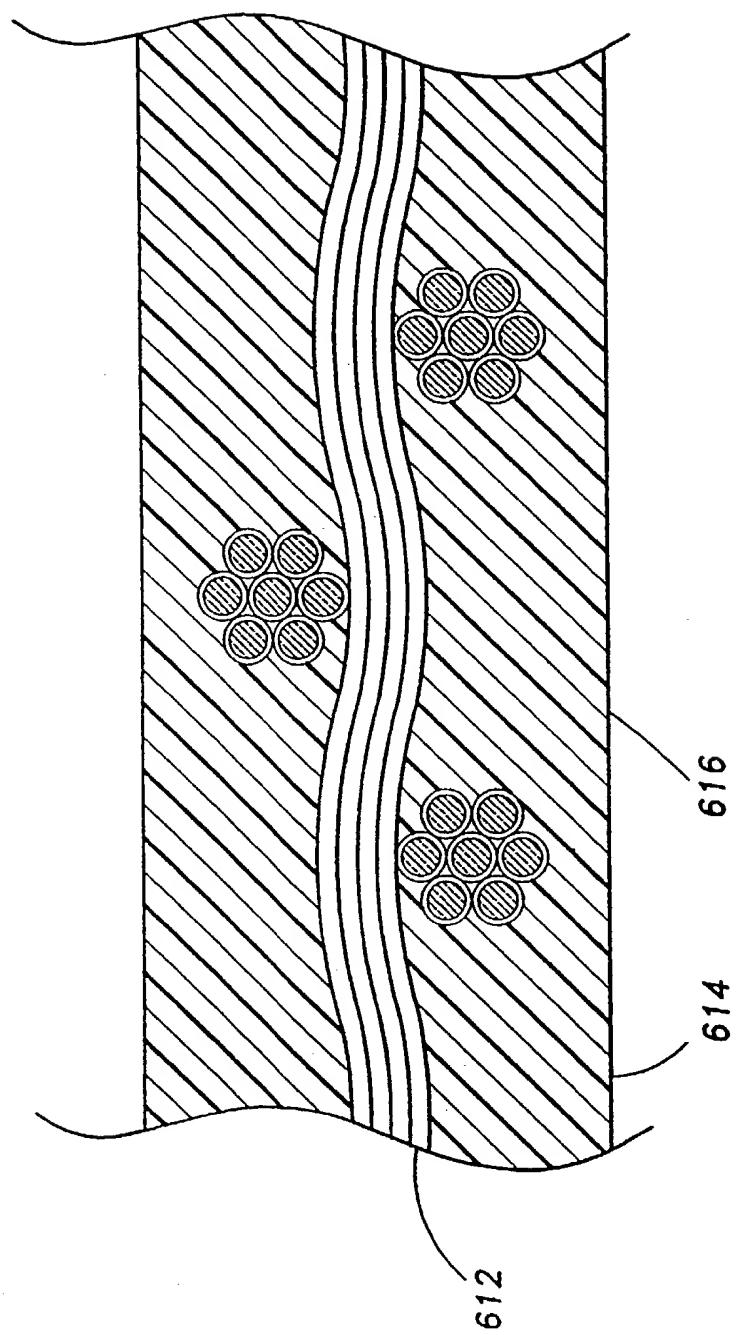


FIG. 6

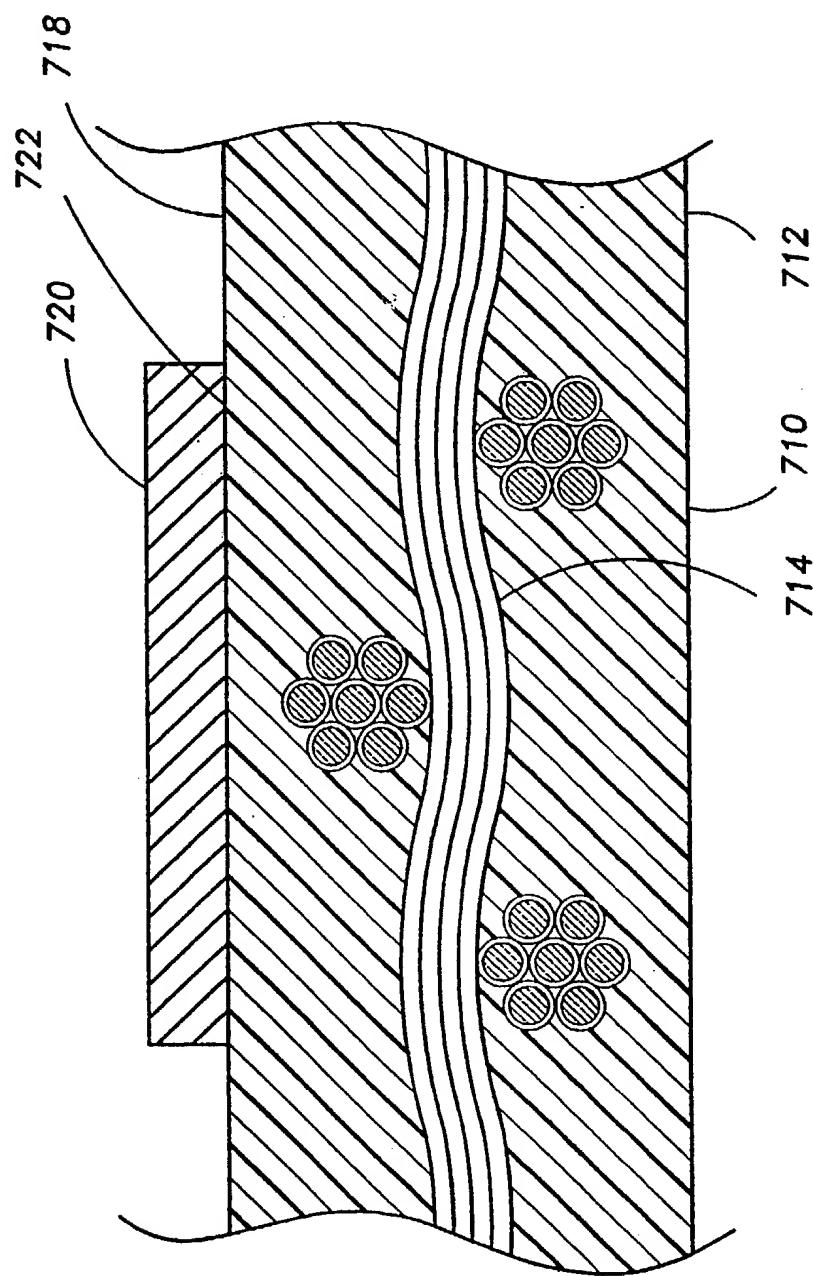


FIG. 7

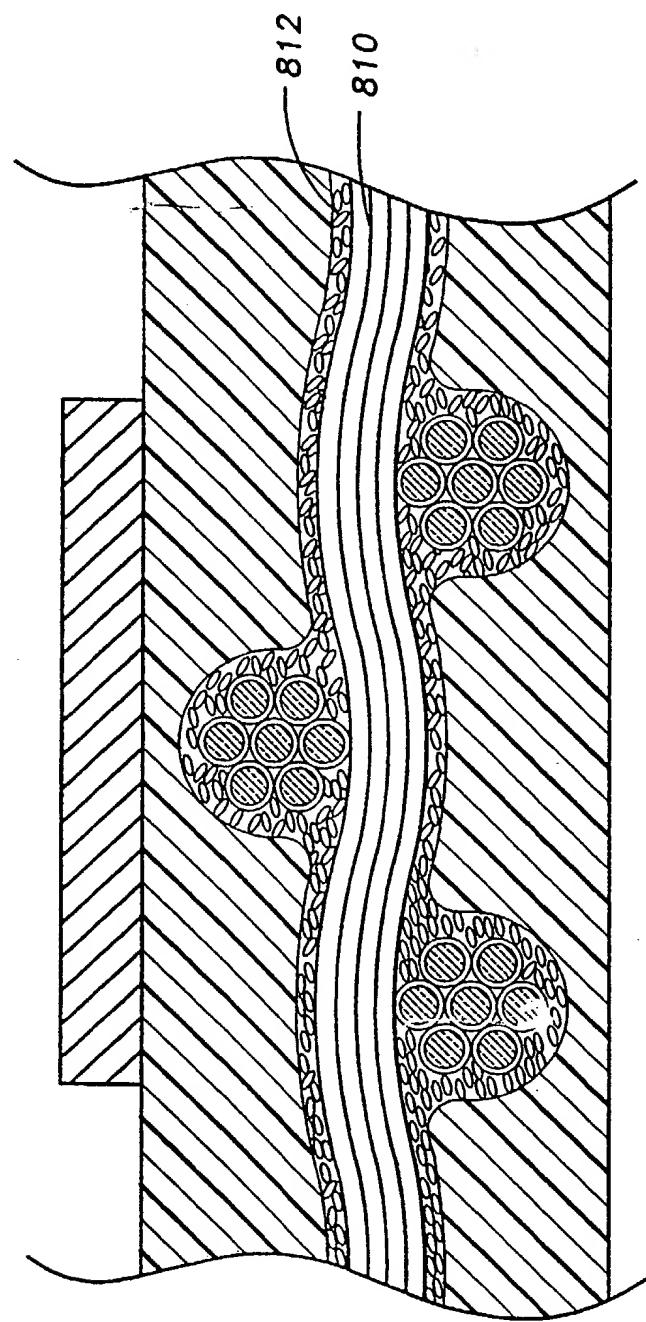


FIG. 8

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 99/21442

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C25/02 C08J5/08 H05K1/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C C08J H05K F16D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	<p>DATABASE INSPEC 'Online! INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB Inspec No. 6242125, NOVICH B E: "Hybon RCY yarns: a laminate reinforcement developed for printed circuit boards" XP002106570 abstract & CIRCUITREE, MARCH 1999, CIRCUITREE, USA, vol. 12, no. 3, page 44, 46, 51 ISSN 1059-843X</p> <p>---</p> <p style="text-align: center;">-/-</p>	1-59

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"8" document member of the same patent family

Date of the actual completion of the international search

31 January 2000

Date of mailing of the international search report

16/02/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Reedijk, A

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/21442

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	DATABASE COMPENDEX 'Online! ENGINEERING INFORMATION, INC., NEW YORK, NY, US NOVICH BRUCE E: "Glass yarn: Sized for better PCB fabrication and properties" Database accession no. EIX99284673861 XP002129270 abstract & PRINT CIRCUIT FABR; PRINTED CIRCUIT FABRICATION 1999 MILLER FREEMAN PUBL INC, SAN FRANCISCO, CA, USA, vol. 22, no. 4, 1999, pages 52-53, ---	1-59
X	US 5 733 823 A (TAIZOU SUGIOKA) 31 March 1998 (1998-03-31) the whole document ---	1-59
A	US 5 217 778 A (G.J. LACHASSE) 8 June 1993 (1993-06-08) abstract ---	1-59
A	US 3 312 569 A (T.E. PHILIPPS ET AL.) 4 April 1967 (1967-04-04) cited in the application claims ---	1-59
A	WO 96 39364 A (PPG INDUSTRIES INC.) 12 December 1996 (1996-12-12) page 5, line 1 - line 13 ---	1-59
A	DATABASE WPI Section Ch, Week 9706 Derwent Publications Ltd., London, GB; Class A85, AN 97-060830 XP002106571 & JP 08 309928 A (HITACHI CHEM CO LTD), 26 November 1996 (1996-11-26) abstract ---	1-59
A	DATABASE WPI Section Ch, Week 9728 Derwent Publications Ltd., London, GB; Class A18, AN 97-306602 XP002106572 & JP 09 118759 A (MATSUSHITA ELECTRIC WORKS LTD), 6 May 1997 (1997-05-06) abstract ---	1-59
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 423 (C-0757), 12 September 1990 (1990-09-12) & JP 02 160944 A (NITTO BOSEKI CO LTD), 20 June 1990 (1990-06-20) abstract ---	1-59

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/21442

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5733823	A 31-03-1998	JP 9077937	A	25-03-1997
US 5217778	A 08-06-1993	BR 8305810	A	29-05-1984
		DE 3338365	A	26-04-1984
		FR 2534995	A	27-04-1984
		GB 2129006	A, B	10-05-1984
		JP 3023775	B	29-03-1991
		JP 59098188	A	06-06-1984
		MX 162613	A	31-05-1991
US 3312569	A 04-04-1967	NONE		
WO 9639364	A 12-12-1996	US 5773146	A	30-06-1998
		CN 1191523	A	26-08-1998
		JP 10510800	T	20-10-1998
JP 8309928	A 26-11-1996	NONE		
JP 9118759	A 06-05-1997	NONE		
JP 02160944	A 20-06-1990	JP 2545957	B	23-10-1996
		DE 68916202	D	21-07-1994
		DE 68916202	T	06-10-1994
		EP 0373871	A	20-06-1990
		US 5206078	A	27-04-1993



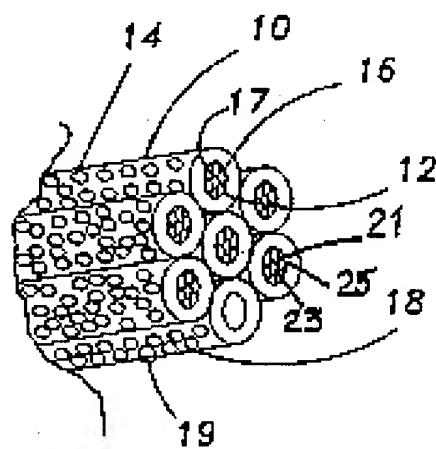


FIG. 1

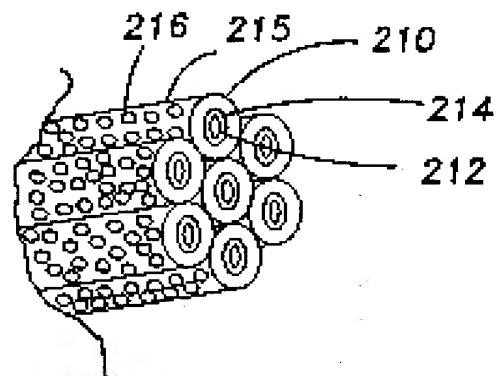


FIG. 2

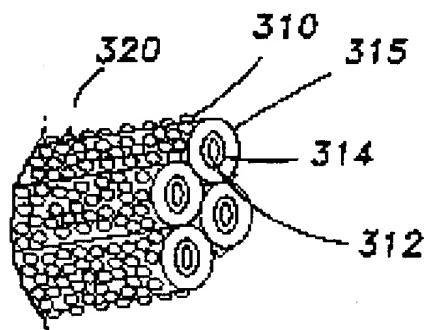


FIG. 3

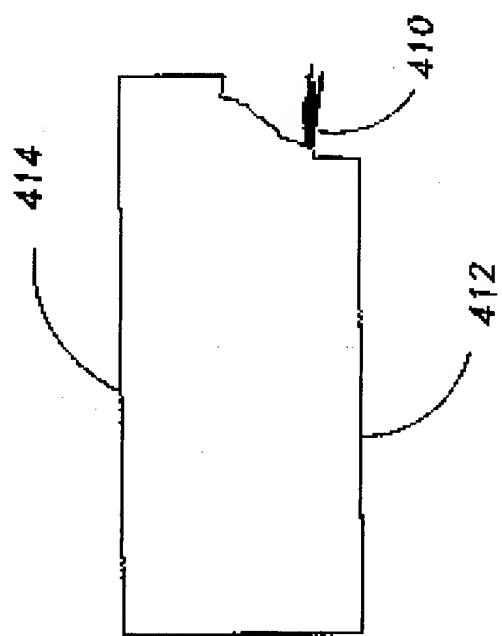


FIG. 4

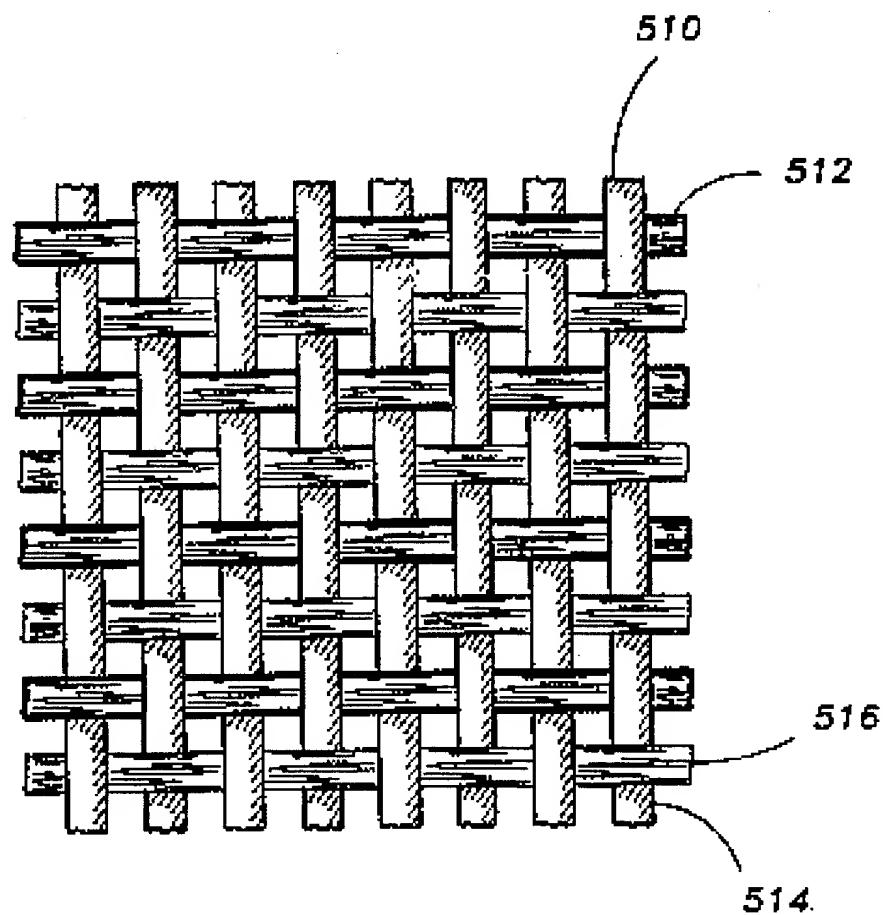


FIG. 5

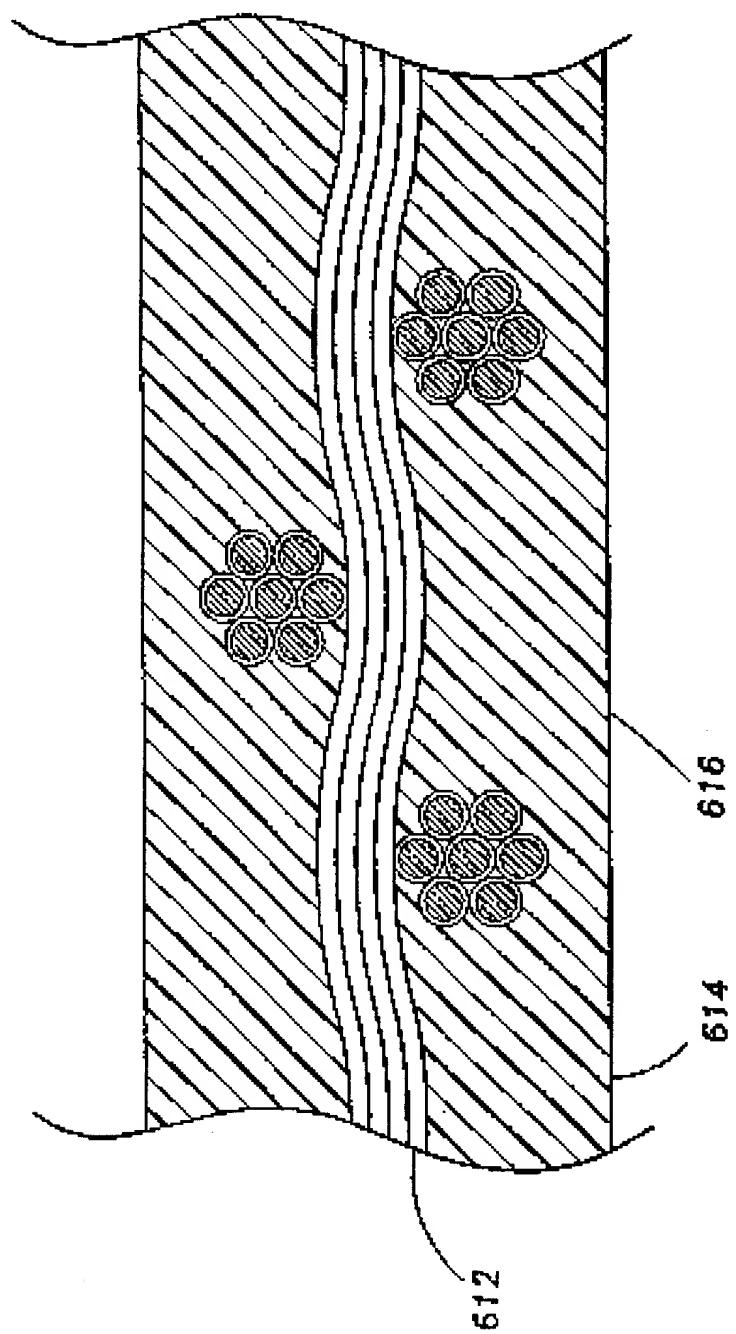


FIG. 6

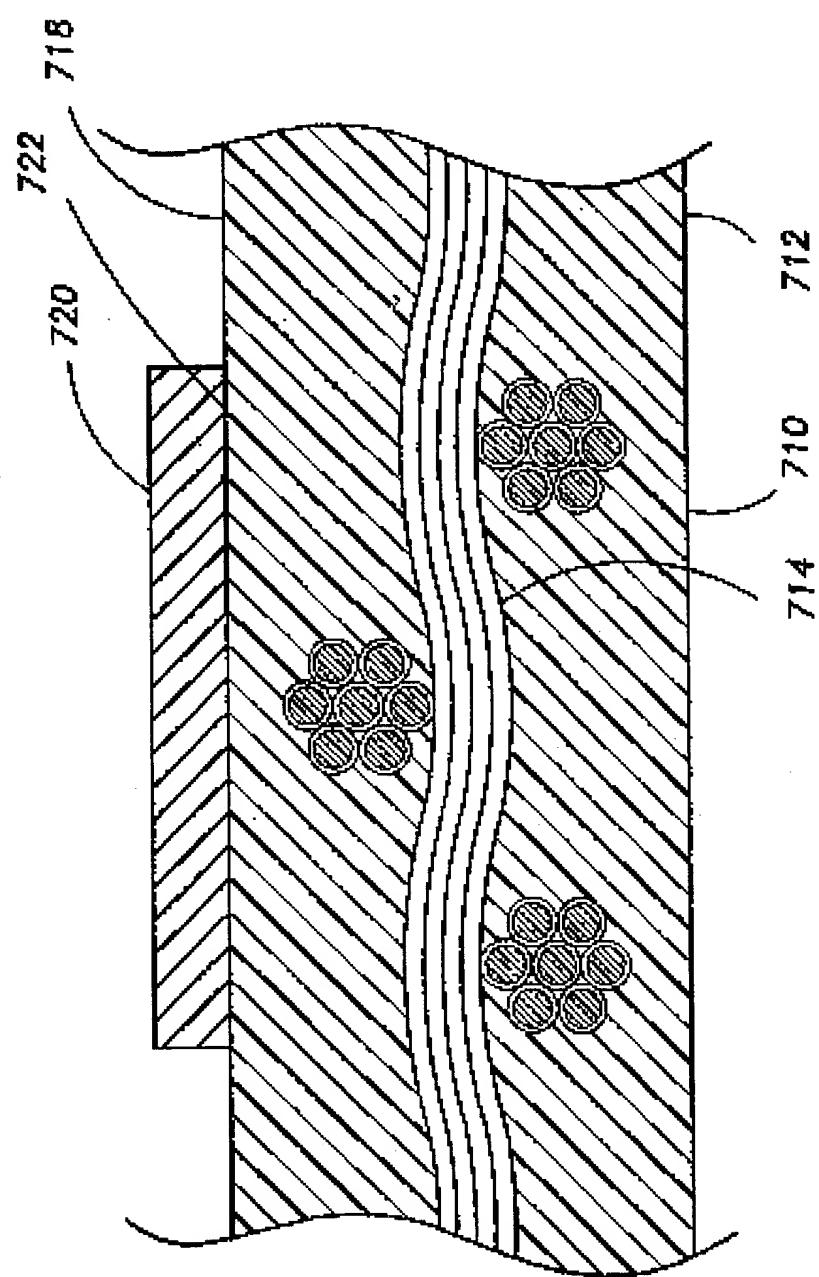


FIG. 7

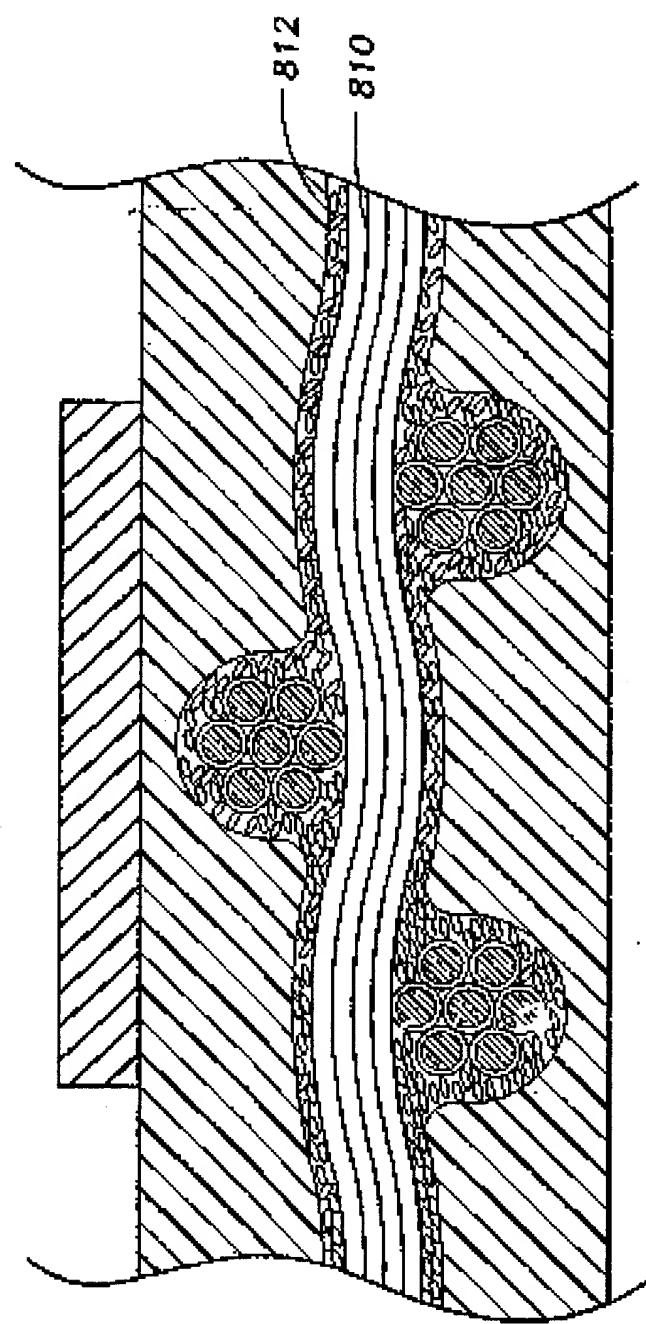


FIG. 8